The Crystal and Molecular Structure of Bis(Pyridoxamine) Copper (II) Dinitrate Monohydrate

Kenneth James Franklin B.Sc. (Hons).

A Thesis

submitted to the Department of Chemistry

in partial fulfillment of the requirements

for the degree of

Master of Science

June 1978

Brock University

St. Catharines, Ontario

Abstract

The crystal structure of $Cu(PM)_2(NO_3)_2 \cdot H_2O$ (where PM is pyridoxamine, $C_8H_{12}N_2O_2$) has been determined from three dimensional x-ray diffraction data. The crystals are triclinic, space group $p\bar{1}$, a = 14.248 (2), b = 8.568 (1), c = 9.319 (1) Å, α = 94.08 (1), β = 89.73 (1), γ = 99.18 (1)°, z = 2, $\mu(MoK_\alpha)$ = 10.90 cm^{-1}, ρ_0 = 1.61 g/cm^3 and ρ_c = 1.61 g/cm^3. The structure was solved by Patterson techniques from data collected on a Picker 4-circle diffractometer to $2\theta_{max}$ = 45°. All atoms, including hydrogens, have been located. Anisotropic thermal parameters have been refined for all non-hydrogen atoms. For the 2390 independent reflections with $F \geq 3\sigma(F)$, R = 0.0408.

The results presented here provide the first detailed structural information of a metal complex with PM itself. The copper atoms are located on centres of symmetry and each is chelated by two PM zwitterions through the amino groups and phenolate oxygen atoms. The zwitterionic form found in this structure involves the loss of a proton from the phenolate group and protonation of the pyridine ring nitrogen atoms. The two independent $Cu(PM)_2$ moieties are symmetrically bridged by a single oxygen atom from one of the nitrate groups. The second nitrate group is not coordinated to the copper atoms but is central to an extensive hydrogen bonding network involving the water molecule and uncoordinated functional groups of PM.

Acknowledgements

The author would like to express his deepest appreciation to Professor M. F. Richardson for her helpful supervision, encouragement and patience during the course of this work.

In addition, thanks should go to Dr. J. M. Miller, Chairman of the Department of Chemistry, the other members of the Department and Dr. D. M. Thompson of Wofford College, South Carolina for their valuable suggestions and assistance. The writer is also grateful to Dr. G. M. Sheldrick for providing the SHELX system of computing programmes which facilitated solution and refinement of this structure and to Mrs. J. Glazebrook and Mr. W. Bell for their assistance in adapting SHELX to the computer systems at Brock University. Special thanks are due Mrs. T. Franklin for providing the crystals.

Financial support for this research was obtained from the National Research Council of Canada and the Ontario Graduate Scholarship Programme.

Table of Contents

List of Tables

List of Figures

Chapter I

Introduction

The class of compounds that we call vitamins was discovered through the realization that certain diseases could be prevented or cured by changes in the diet. That such relationships existed has been known for hundreds of years. For example, the therapeutic value of animal liver towards night blindness was recognized by ancient Greek, Roman and Arab physicians (1). History also records that citrus fruits were used by sailors to prevent scurvy during their long voyages at sea. However, it is only within the past century that substances not classified as fats, carbohydrates, proteins or minerals were found to be essential for life.

The term, vitamine (L. vita + amine), was applied to these unknown compounds by Funk (1) in 1912 who believed these dietary factors to be nitrogenous. This word was later shortened to vitamin when it was discovered that not all these essential factors contained nitrogen.

Vitamin B was originally termed the "anti-beriberi factor" as a result of investigations by Eijkman (2) who produced polyneuritis (beriberi) in fowl fed polished rice and effected a cure by adding rice bran to their diet. As a result of further study and improved techniques, it was found that vitamin B was not a single compound but a mixture of vitamins. In 1934, György (3) added concentrates of thiamine (B_1) and riboflavine (B_2), known components of the vitamin B complex, to a vitamin B deficient ration being fed to rats. He found that poor growth and a type of dermatitis called acrodynia resulted from this diet and that these symptoms could be prevented by feeding other sources of the vitamin B complex. György

termed this unknown component vitamin B_6 (3).

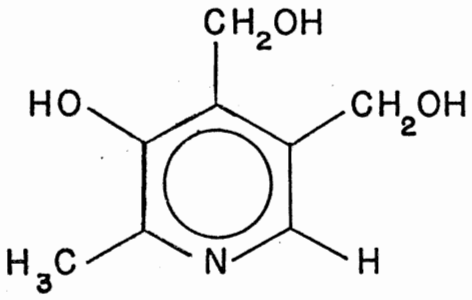
In 1938, several research groups (4-6) reported the isolation of crystalline vitamin B_6. The processes of degradation and synthesis by which this compound was characterized as pyridoxol (see figure 1) have been described by Wagner and Folkers (7). Later investigations by Snell (3) revealed that a number of related compounds also produced vitamin B_6 activity and today there are several compounds known collectively as pyridoxine or vitamin B_6 (see Figure 1).

This hectic research activity continued into the 1940's when it became evident that vitamins played important roles in several enzymatic reactions. Enzymes, which act as biological catalysts, are composed of an apoenzyme or protein portion and a cofactor portion. The latter may be an inorganic divalent ion (activator) such as Ca(II), Mg(II) or Zn(II) or an organic molecule (coenzyme) such as a vitamin derivative.

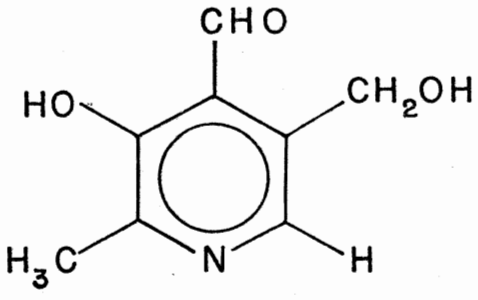
The coenzyme form of vitamin B_6 is pyridoxal phosphate (PLP) or codecarboxylase. In this form, vitamin B_6 is involved in a variety of the enzymatic transformations and metabolic reactions of amino acids. These reactions include transamination, decarboxylation, condensation, substitution and racemization reactions which serve to modify the structural skeletons of amino acids (8). Enzymes incorporating PLP also contribute to the biosynthesis and metabolism of sulphur-containing amino acids, tryptophan, nicotinic acid, riboflavine and folic acid (8).

The sequence of these enzymatic reactions is shown schematically in Figure 2. The first step involves binding of PLP to the apoenzyme and a Schiff base condensation of PLP and the ε amino group of a lysine residue to form the holoenzyme (I). Biochemical studies involving resolution and

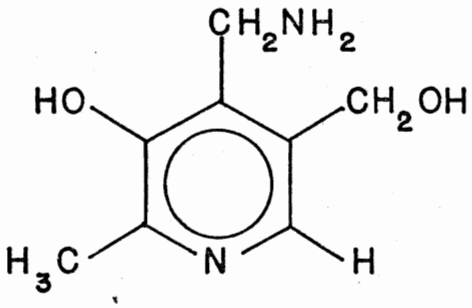
FIGURE I. FORMS OF VITAMIN B_6



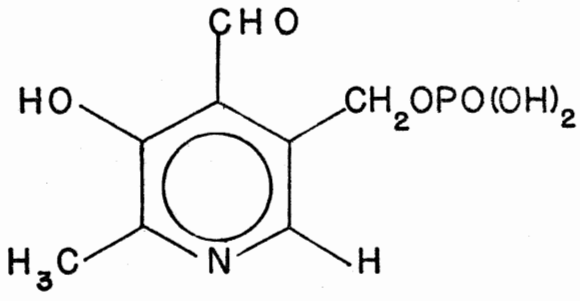
PYRIDOXINE (PN)
(ALSO PYRIDOXOL)



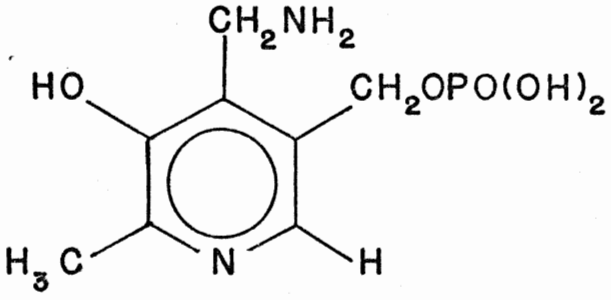
PYRIDOXAL (PL)



PYRIDOXAMINE (PM)

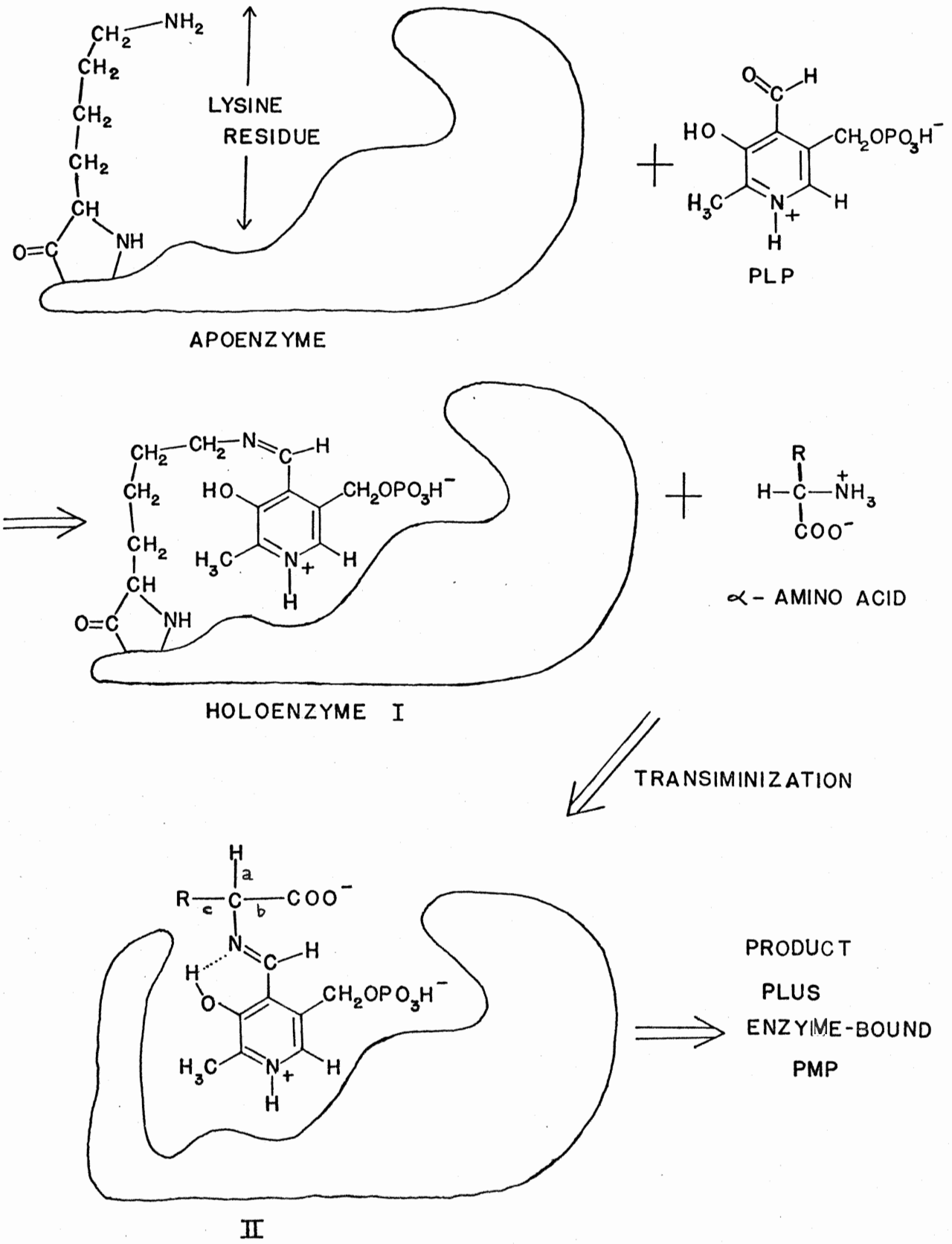


PYRIDOXAL PHOSPHATE (PLP)
(ALSO CODECARBOXYLASE)



PYRIDOXAMINE PHOSPHATE
(PMP)

FIGURE 2. SCHEMATIC DIAGRAM OF ENZYMATIC REACTIONS INVOLVING VITAMIN B_6



reactivation of holoenzymes suggest that a rapid association is followed by a much slower conformational change (9). The latter is probably due to interactions between various protein sites and substituents on the pyridine ring. In fact, it has been shown that each functional group contributes to the binding of the coenzyme (10). The imine bond itself is not of primary importance in bonding since it is broken in the next step and since certain apoenzymes can be fully activated by PMP (11).

The holoenzyme then reacts with the incoming α-amino acid which displaces the lysyl residue to form a second Schiff base (II). The formation of this complex labilizes the bonds to the α-carbon labelled a, b and c. The weakening of these bonds is effected by the imine double bond which is in conjugation with a protonated pyridine ring. Many of the reactions involving PLP-dependent enzymes can be classified in terms of which of these bonds is actually broken (11).

The formation of a complex such as II appears to be common to most enzymes incorporating PLP. The fact that a given enzyme catalyzes only one reaction type can be explained by considering the conformation of the groups attached to the α-carbon (12). As the sigma bond is broken, the electron density in the delocalized π system of the Schiff base is increased. In order to lower the energy of the transition state, the bond to the leaving group should be perpendicular to the plane of the Schiff base. The orientation required for a particular reaction is determined by the structure of the binding sites in different enzymes (12). The stereochemical aspects of PLP catalysis have been reviewed by Dunathan (13).

After bond cleavage, the ketimine form of the Schiff base undergoes hydrolysis to form product and enzyme bound PMP. The latter may undergo a reverse reaction with an α-keto acid to regenerate PLP.

From the above discussion, it can be seen that the catalytic effect of enzymes is due to several features (14). By selectively binding PLP, and probably the amino acid as well, the enzyme serves to increase the local concentration of reactants. The various side chains present at the active site can produce solvent effects resulting in an increase or decrease in the strength of an acid. Such effects can also lower the redox potential difference between reactants and products. The enzyme may also participate in the general acid catalysis of the condensation reaction between PLP and the lysine residue. The resulting formation of an imine bond facilitates addition of the amino acid. The effect of the enzyme on stabilization of the transition state has already been mentioned. However, the planarity of the complex itself may also be influenced by the enzyme. Finally, the enzyme may act directly to provide the excitation energy for the reaction (14).

Much of the current understanding of these enzymatic processes has been derived from the study of model reactions where metal ions replace the enzyme (15). Perhaps the most successful model system is the transamination reaction shown schematically in Figure 3. An α-amino acid, PL and a metal ion react to form an aldimine Schiff base complex which passes through a resonance stabilized intermediate to form a ketimine complex. The latter then dissociates to give PM, metal ion plus the α-keto acid. Longenecker and Snell (16) have suggested that the metal ion in this and other model reactions could serve one or more of the following catalytic functions:

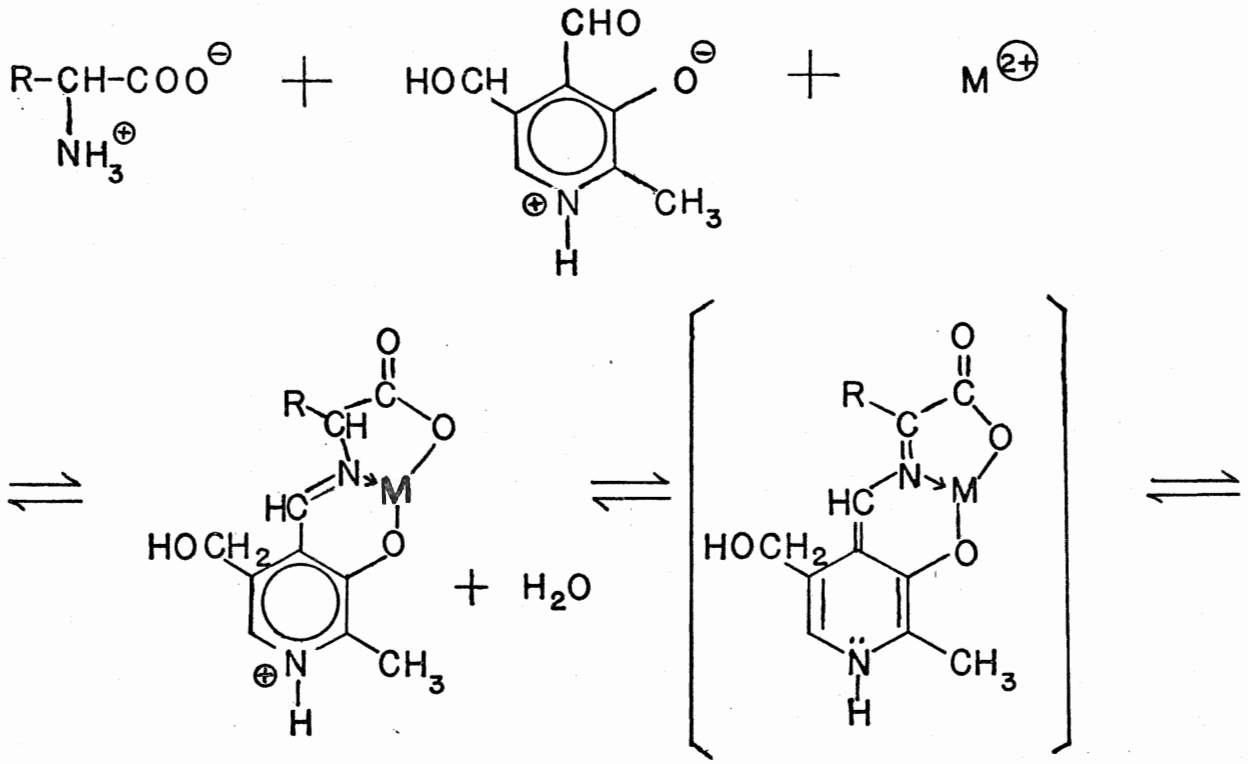
(a) act as a template to assist the formation of the Schiff base,

(b) stabilize the Schiff base and thus promote its formation,

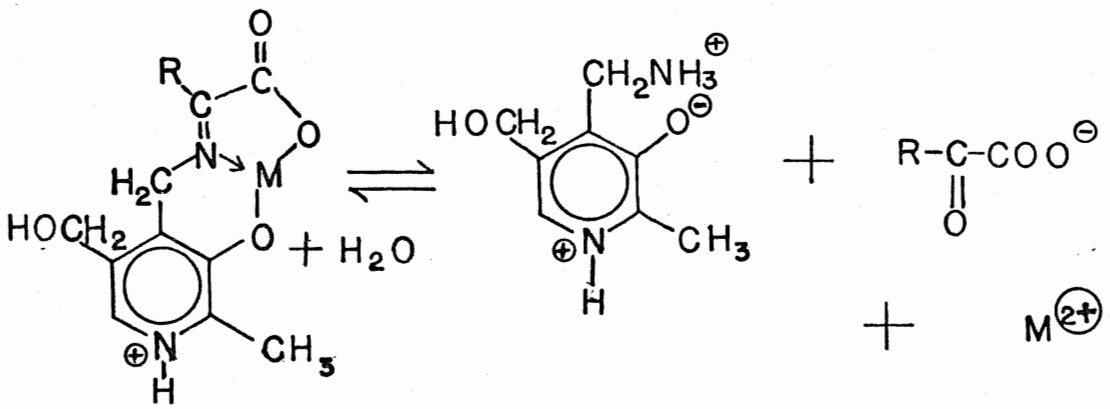
(c) maintain planarity of the conjugated double bonds to facilitate electron transfer,

(d) reinforce the withdrawal of electrons from the α-carbon.

FIGURE 3.
THE TRANSAMINATION REACTION



ALDIMINE SCHIFF BASE COMPLEX



KETIMINE SCHIFF BASE COMPLEX

With respect to the first of these, a number of workers (17-19) have found experimental evidence that metal ions trap preformed Schiff base rather than providing a kinetic template for its formation. Metal-independent paths for Schiff base formation have been found for Cu, Ni and Co while both metal-independent and metal-dependent paths exist for Mg, Mn, Zn, Cd and Pb (20,21).

Hopgood and Leussing (21) found that for divalent metal ions, the order of catalytic efficiency was Pb >> Cd > Mn ∿ Mg > Zn >> Co, Ni, Cu (very small). It was noted that the metal ions most effective as catalysts are those with no partly filled d orbitals. Complexes of these ions with ammonia tend to be more labile than those of the catalytically inactive Co, Ni and Cu. At the same time, such complexes do not necessarily conform to particular geometries, which in ions with incompleted subshells are stabilized by ligand field effects. Since a fixed spatial orientation of the reactants to the metal ion causes inactivity, Hopgood and Leussing (21) suggest that the term promnastic (Gr. matchmaker) rather than template be used to describe the effect of a catalytic agent which forms a ternary complex with two reactants but which imposes a minimum steric requirement on them. These authors (21) also point out that Schiff bases are unstable in acidic solution and that metal ions, whether kinetically active or not, are necessary for the formation of observable amounts at equilibrium. Thus, although the model mechanisms are not fully understood, it would appear that at least some metal ions do assist Schiff base formation in a manner similar to that found in enzymes (22).

The reaction specificity of enzymatic systems is difficult to achieve in model systems although a few examples exist. Thanassi (23) has shown

that substitution at the α-carbon of α-aminomalonates can affect reaction pathways in the 5-deoxypyridoxal catalyzed reactions of these compounds. The electronegativity of the leaving group has been found to be critical in determining whether β-elimination predominates over other vitamin B_6 catalyzed reactions (24). Tenenbaum, Withrup and Abbot (25) have demonstrated selective deuteration at the α and β positions of amino acids. The selectivity of this reaction, which is catalyzed by Al^{3+} and PL was attributed to the pH dependence of the reactivity of the dihydropyridine intermediate. Finally, Blum and Thanassi (26) have found that the choice and concentration of metal ion can result in reaction specificity. They suggest (26) that the metal ion is able to impose the steric control necessary to promote the mechanism of reaction specificity proposed by Dunathan (13) (vide supra).

X-ray crystallography has been used to investigate the stereochemistry of Schiff base complexes. Solid compounds were first isolated by Christensen (27) who found a 2:1 ligand to metal ratio for Mn(II), Ni(II), Zn(II), Fe(II) and Fe(III) but a 1:1 ratio in the case of Cu(II). The crystal structures of two copper complexes (28,29) revealed that the amino acid and vitamin moieties are approximately coplanar, occupying three sites in the square pyramidal geometry. This supports the suggestion (16) that the metal ion serves to maintain the planarity of the conjugated system and thus facilitate electron transfer. In contrast, the metal ions Mn(II), Ni(II) and Zn(II) form 2:1 complexes in which the metal is octahedrally coordinated and the Schiff base is non-planar (30,31).

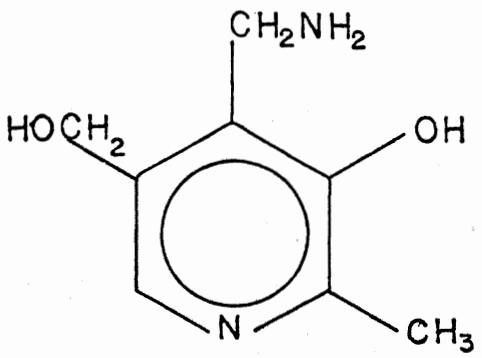
These results are particularly interesting in view of the fact that Cu(II) has a very small catalytic effect on Schiff base formation but is

relatively very active in promoting the non-enzymatic transamination reaction. It would seem that both these effects can be attributed to the steric requirements of the unfilled d orbitals in Cu(II). That is, these requirements do not permit the promnastic mechanism proposed (21) for the former reaction but do fulfill the necessity of steric rigidity in the transition state of the latter.

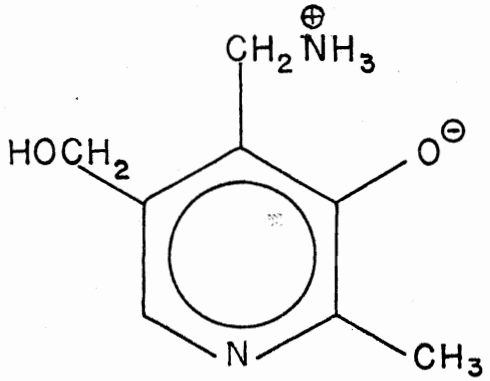
The extension of this hypothesis to other metals is dependent on the results of further experimentation, especially additional structure determinations. It is known that the comparative activities of metal ions in model transamination reactions follow the order (31): Ga(III) > Cu(II) > Al(III) > Fe(II) > Fe(III) $\gtrsim$ Zn(II) > In(III) $\gtrsim$ Ni(II) > Cd(II) > Sc(III). The interpretation of this catalytic order is still being formulated (32) although as early as 1957, Longenecker and Snell (16) realized that the order of metal ion activities closely parallels the stabilities of chelates for these metals with PM and other ligands. This observation plus the suggestion (33) that PM chelates of metals have a role in the dissociation of the ketimine Schiff base (see Figure 3) has resulted in a number of studies involving PM and metal ions alone.

In PM, there are several potential binding sites: the heterocyclic nitrogen, the phenolic oxygen, the hydroxymethyl oxygen and the aminomethyl nitrogen. Chelation of metal ions by the phenolic and amino groups to form a stable six-membered ring can also occur. The type of complexation which takes place is dependent on which form of PM dominates (see Figure 4). It is thought that PM normally exists in solution as zwitterion II (34) which would be incapable of chelation due to protonation of the amino group. Thus, if a chelate complex exists as proposed (33) for model transamination

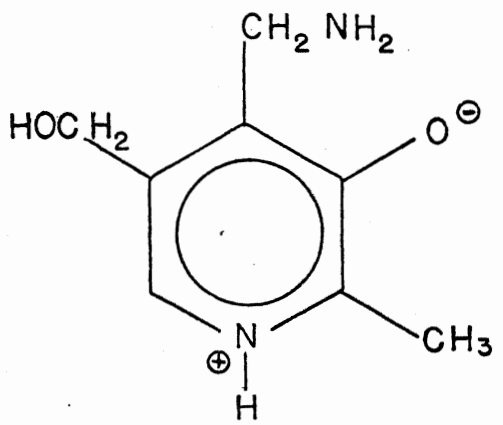
FIGURE 4. FORMS OF PYRIDOXAMINE



I



II



III

reactions, form II must be converted to the non-polar form I or to the new zwitterion III.

Williams and Neilands (35) studied the interaction of PM with metal ions by titrating from acidic to basic solution in the presence of Cu(II), Fe(II), Fe(III), Al(III) and Mg(II). It was shown that the only metal ion effectively chelated by PM was Cu(II). The formula of the complex was determined spectrophotometrically to be $Cu(PM)_2$ (35). The high affinity of PM for Cu(II) was also observed by other authors (36,37). Matsushima and Martell (38) obtained clear, stable absorption spectra for PM complexes containing Zn(II), Cu(II) and Ni(II) in methanol. The instability of Mn(II) and Co(II) complexes was attributed to oxidation-reduction reactions involving the metal ion. Results of a recent study using polarographic methods indicate that monodentate coordination through the heterocyclic nitrogen may be present in a Zn(II) complex although chelate formation was found for the corresponding Cd(II) complex (39,40).

Chelation of metal ions by PM has been postulated by many of the above authors whose results compare favourably with studies of Schiff base complexes. However, in contrast to the latter where structure determinations have been completed, little is known about the structure of the PM molecule (particularly with respect to protonation of the heterocyclic nitrogen atom) in metal-PM complexes. The following results provide the first detailed structural information of a metal complex with PM itself.

Chapter II

Experimental

A. Crystal Selection and Density Determination

Dark green crystals of $Cu(PM)_2(NO_3)_2 \cdot H_2O$ were obtained by Mrs. T. Franklin from the evaporation of an equimolar solution of pyridoxamine (PM) and copper (II) nitrate in water. Plate-shaped crystals suitable for further study by x-ray diffraction were chosen with the aid of a polarizing microscope. The selection was based on clarity, size, regularity of shape and the sharpness of the extinctions when the crystal was rotated in plane polarized light.

Several crystals were mounted on thin glass fibres with Lepage's Five Minute Epoxy cement. One of these was used by Mrs. T. Franklin for preliminary photographic studies. However, the doubling of spots on upper layer Weissenberg photographs indicated that the crystal was actually twinned. A second crystal, with the dimensions 0.43 x 0.15 x 0.03 mm, was found to be suitable for the complete x-ray structure determination.

Following the selection of suitable crystals, the density of $Cu(PM)_2(NO_3)_2 \cdot H_2O$ was determined by Mrs. T. Franklin to be 1.61 g cm^{-3}. The flotation technique used in this determination is fully described elsewhere (41).

B. Photographic Studies

Oscillation photographs were taken on a Picker x-ray diffraction instrument using a Weissenberg camera from Charles Supper Co. and No-Screen Medical X-ray Film from Kodak. Fifteen minute exposures to

CuK_α radiation were used for all photographs. The oscillation range of the crystal was 15°. The films were processed using Rapid X-ray Developer and X-ray Fixer from Kodak. Alignment of the crystal was accomplished by the methods outlined in Stout and Jensen (42).

Once the crystal was aligned, the above apparatus was used to take equi-inclination Weissenberg photographs. Nickel filtered CuK_α radiation (λ = 1.5481 Å) and exposure times of eleven to sixteen hours were used for all photographs. The h0ℓ, h1ℓ, h2ℓ and h3ℓ layers were photographed using camera settings based on the lattice dimensions obtained from the oscillation photographs (43).

The crystal was transferred to a precession camera (Charles Supper Co.) and aligned (44) using unfiltered CuK_α radiation. Photographs of the 0kℓ, 1kℓ, 2kℓ, hk0 and hk1 layers were then taken using a nickel filter and exposure times of eight to twelve hours. Calculations of camera settings for non-zero layers followed Buerger (45).

The lack of symmetry, of systematic absences and of orthogonal axes indicated that the crystal was triclinic. Axes were chosen such that the reciprocal unit cell angles α^*, β^* and γ^* were all less than 90°. The photographs were indexed on this basis and it was found that reflections having odd values of k were systematically weak. This observation was attributed to a "pseudo" translational symmetry element along the y axis.

C. Diffractometer Studies

The crystal was transferred to a Picker Four-Circle Diffractometer. The methods of crystal alignment given in Stout and Jensen (46) were employed. Zirconium filtered MoK_α radiation (λ = 0.7107 Å) was used for all diffractometer studies.

Accurate reciprocal unit cell dimensions were obtained from 2θ values measured on the diffractometer. Peak profiles were obtained by taking ten second counts at small increments (0.02 to 0.05°) of 2θ. The centre of the reflection was found by averaging the half-height values. This procedure was then repeated for the reflection at -2θ and the results were averaged to give a value used in the calculations. Several measurements were used in the determination of each parameter.

The accuracy of the results was further enhanced by the sharp definition of the reflections where permitted by resolution of the MoK_{α_1} (λ = 0.70926 Å) and MoK_{α_2} (λ = 0.71354 Å) doublet. Whenever possible, both values were used in the calculations. Both the reciprocal cell lengths, a^*, b^* and c^*, and the corresponding angles, α^*, β^* and γ^* were calculated by equation (1) (47).

$$\frac{\sin\theta}{\lambda} = \frac{1}{2}[h^2a^{*2} + k^2b^{*2} + \ell^2c^{*2} + 2hka^*b^*\cos\gamma^* + 2h\ell a^*c^*\cos\beta^* + 2k\ell b^*c^*\cos\alpha^*]^{\frac{1}{2}}$$

A summary of these results is presented in Table 1. The direct cell constants were found (48) to be a = 14.248 (2), b = 8.568 (1), c = 9.319 (1) Å, α = 94.08 (1), β = 89.73 (1) and γ = 99.13 (1)° where the estimated standard deviation in the last figure is given in parentheses. Assuming 2 molecules per unit cell, the calculated density is 1.61 g cm^{-3}.

Data collection took place in two stages, first of all to a maximum 2θ of 35° which permitted solution of the structure and later to 45° to allow location of hydrogen atoms and final refinement. All the data were collected from the same crystal using the ω - 2θ scan technique, with ω changing to one half the rate of 2θ. The scan rate was 1° per minute over a 1.3° range centred on calculated peak positions. For very intense reflections, the peak counting rate was reduced to below 40,000 cps by inserting 0.013 mm

Table 1. Determination of Unit Cell Dimensions

a* axis (n 0 0 reflections)

n	2θ	d^*_{100}	n	2θ	d^*_{100}
5(α_1)	14.484	0.071096	11(α_1)	32.204	0.071097
5(α_2)	14.567	0.071070	11(α_2)	32.399	0.071089
6(α_1)	17.398	0.071078	12(α_1)	35.214	0.071081
6(α_2)	17.501	0.071069	12(α_2)	35.440	0.071094
8(α_1)	23.270	0.071085	13(α_1)	38.266	0.071094
8(α_2)	23.386	0.071006†	13(α_2)	38.502	0.071088
9(α_1)	26.224	0.071079	16(α_1)	47.578	0.071090
9(α_2)	26.386	0.071078	16(α_2)	47.871	0.071073
10(α_1)	29.202	0.071086	17(α_1)	50.760	0.071096
10(α_2)	29.380	0.071080	17(α_2)	51.078	0.071083

$a^* = \bar{d}^*_{100} = 0.071085\ (\pm 2 \times 10^{-6})\ \text{Å}^{-1}$

† The α_2 component of the 800 reflection was poorly resolved and the average value does not include the tabulated result. Rejection of this value was further supported by standard statistical considerations.

b* axis (0 n 0 reflections)

n	2θ	d^*_{010}	n	2θ	d^*_{010}
1	4.828	0.11854	4(α_1)	19.358	0.11852
2(α_1)	9.647	0.11856	4(α_2)	19.466	0.11846
2(α_2)	9.697	0.11846	6(α_1)	29.216	0.11853
3(α_1)	14.485	0.11850	6(α_2)	29.385	0.11848
3(α_2)	14.574	0.11851			

$b^* = \bar{d}^*_{010} = 0.11851\ (\pm 1 \times 10^{-5})\ \text{Å}^{-1}$

c* axis (0 0 n reflections)

n	2θ	d^*_{001}	n	2θ	d^*_{001}
1	4.392	0.10784†	6(α_1)	26.469	0.10759
2	8.766	0.10754	6(α_2)	26.631	0.10759
3	13.144	0.10736†	7(α_1)	30.979	0.10758
4(α_1)	17.566	0.10764	7(α_2)	31.172	0.10759
4(α_2)	17.654	0.10753	8(α_1)	35.544	0.10759
5(α_1)	22.002	0.10762	8(α_2)	35.762	0.10758
5(α_2)	22.124	0.10756			

$c^* = \bar{d}^*_{001} = 0.10758\ (\pm 1 \times 10^{-5})\text{Å}^{-1}$

† These values were not used in the calculation of the average value. Rejection was based on standard statistical considerations.

Table 1. (continued)

α^* (0 k ℓ reflections)

k	ℓ	2θ	cos α^*	k	ℓ	2θ	cos α^*
6	$-4(\alpha_1)$	33.148	0.071521	6	-6	38.336	0.070844
6	$-4(\alpha_2)$	33.344	0.072159	6	-6	38.592	0.070143
4	$-5(\alpha_1)$	28.378	0.071207	-4	4	25.282	0.071341
4	$-5(\alpha_2)$	28.532	0.072548	-4	4	25.426	0.072142
4	$-6(\alpha_1)$	31.828	0.071193	4	4	27.172	0.070705
4	$-6(\alpha_2)$	32.202	0.071503	4	4	27.336	0.070463

$\overline{\cos \alpha^*} = 0.07131\ (\pm 2.1 \times 10^{-4})$

$\alpha^* = 85.91\ (\pm 0.01)°$

$$\cos \alpha^* = \frac{1}{2k\ell b^* c^*} \left| \frac{4\sin^2 \theta}{\lambda^2} - k^2 b^{*2} - \ell^2 c^{*2} \right|$$

β^* (h 0 ℓ reflections)

h	ℓ	2θ	cos β^*	h	ℓ	2θ	cos β^*
6	$4(\alpha_1)$	24.904	0.0070554	7	$4(\alpha_1)$	27.072	0.0077120
6	$4(\alpha_2)$	25.056	0.0079590	7	$4(\alpha_2)$	27.246	0.0070510
4	$3(\alpha_1)$	17.611	0.0071300	6	$-4(\alpha_1)$	24.720	0.0067495
4	$3(\alpha_2)$	17.697	0.0047300	6	$-4(\alpha_2)$	24.879	0.0069945
10	$6(\alpha_1)$	39.955	0.0066831	10	$8(\alpha_1)$	46.466	0.0071667
10	$6(\alpha_2)$	40.211	0.0069012	10	$8(\alpha_2)$	46.764	0.0071470

$\overline{\cos \beta^*} = 0.006765\ (\pm 1.9 \times 10^{-4})$

$\beta^* = 89.61\ (\pm 0.01)°$

$$\cos \beta^* = \frac{1}{2h\ell a^* c^*} \left| \frac{4\sin^2 \theta}{\lambda^2} - h^2 a^{*2} - \ell^2 c^{*2} \right|$$

γ^* (h k 0 reflections)

h	k	2θ	cos γ^*	h	k	2θ	cos γ^*
6	$4(\alpha_1)$	28.168	0.15888	-10	$4(\alpha_1)$	32.512	0.15867
6	$4(\alpha_2)$	28.308	0.15614	-10	$4(\alpha_2)$	32.718	0.15840
10	$4(\alpha_1)$	37.864	0.15874	-8	$4(\alpha_1)$	27.910	0.15891
10	$4(\alpha_2)$	38.101	0.15876	-8	$4(\alpha_2)$	28.081	0.15893
8	$4(\alpha_1)$	32.807	0.15957	-10	$8(\alpha_1)$	45.508	0.15923
8	$4(\alpha_2)$	33.008	0.15939	-10	$8(\alpha_2)$	45.508	0.15923
-6	$4(\alpha_1)$	23.953	0.15882				
-6	$4(\alpha_2)$	24.092	0.15931				

$\overline{\cos \gamma^*} = 0.15877\ (\pm 2.2 \times 10^{-4})$

$\gamma^* = 80.86\ (\pm 0.01)°$

$$\cos \gamma^* = \frac{1}{2hka^* b^*} \left| \frac{4\sin^2 \theta}{\lambda^2} - h^2 a^{*2} - k^2 b^{*2} \right|$$

zirconium filters in the reflected beam. Background intensities were counted for ten seconds at each end of the scan.

The intensity of a standard reflection, (-5,2,1) was measured at one hour intervals in order to monitor instrumental fluctuation and possible crystal decomposition. Although more than a year separated the two sets of data collection, there was no significant drop in the intensity of the standard indicating the overall stability of the crystal. Minor fluctuations were attributable to instrumental instability resulting from variations in humidity and temperature.

D. Data Reduction

The net intensity of a reflection was computed by equation (2):

$$N_p = N_T - 4(N_{B_1} + N_{B_2}) \qquad (2)$$

where N_p, N_T, N_{B_1} and N_{B_2} are the net, the total and two background counts respectively. The data between successive measurements of the standard were corrected according to the number of intervening reflections. All data were normalized to the initial intensity of the standard reflection. In cases where extra filters had been used, the measured intensity was multiplied by a factor of the form 10^{ax} where x is the number of filters and a (= 0.0549) was an empirical constant.

Lorentz and polarizing corrections were applied to convert the net intensities, I, into structure factors by equation (3):

$$F\ (hk\ell) = \left(\frac{I(hk\ell)}{Lp}\right)^{\frac{1}{2}} \qquad (3)$$

The combined form of the Lorentz and polarizing factors, Lp, is given by equation (4) for 4-circle diffractometer data:

$$Lp = \frac{1 + \cos^2 2\theta}{\sin 2\theta} \qquad (4)$$

where θ is the Bragg angle of the hkℓ reflection. No corrections were made for extinction or absorption ($\mu(MoK_\alpha) = 10.90\ cm^{-1}$).

Initially, for the data to 35°, standard deviations were calculated by the procedure detailed in Stout and Jensen (49):

$$\sigma(F) = (Lp)^{-\frac{1}{2}} \frac{N_T + r^2 N_B + (kN_p)^2}{N_T - N_B}^{\frac{1}{2}} \qquad (5)$$

where r (= 4) is the ratio of the scan time to the total time required to take two background counts and k, a constant, was set to 0.05. The value of $1/\sigma^2(F)$ is often used as a weight factor for the reflection data. In the latter stages of the structure refinement, it became possible to refine the weighting scheme (vide infra) and for calculations using the complete data set, k was set to 0.00. The value of F was set to 0.01 and $\sigma(F)$ to 1000 for reflections with no net intensity.

A total of 2931 reflections were measured having $2\theta \leq 45°$. Of these, 2390 had $F \geq 3\sigma(F)$ and were classified as observable. The remaining 541 unobserved reflections were assigned zero weights during the refinement procedures and were not included in the R-factor calculations. In the programme SHELX (55), which was used for the actual refinement of the structure, the scattering factors were calculated from the analytical expression (5):

$$f(\lambda^{-1}\sin\theta) = \sum_{i=1}^{4} a_i \exp(-b_i \lambda^{-2} \sin^2\theta) + c \qquad (6)$$

The coefficients a_i, b_i and c for Cu, C, H, N and O as well as the real and imaginary parts of the corrections for anomalous dispersion were taken from the International Tables for X-ray Crystallography (50).

Chapter III

Structure Determination and Refinement

A. The Heavy Atom Method

Using the initial data set to 35%, a three-dimensional unsharpened Patterson function was calculated by:

$$P(u,v,w) = \Sigma\Sigma\Sigma|F_0(hk\ell)|^2 \cos 2\pi (hu + kv + \ell w) \qquad (7)$$

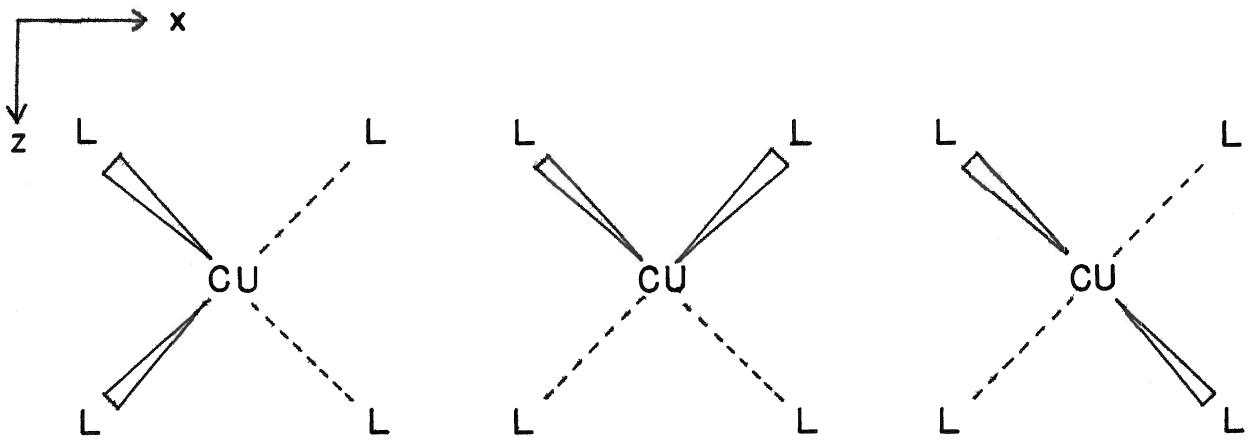
where u, v, w are the fractional coordinates of the cell at which the function was calculated and $|F_0(hk\ell)|$ is the absolute value of the observed structure factor for the $hk\ell$ plane. The peaks on a Patterson map correspond to interatomic vectors with the relative height of the peak being proportional to the product of the number of electrons of the two atoms involved. The twenty highest peaks are listed in Table 2.

The calculated height of a Cu-Cu peak relative to the origin is 344. No peaks of this intensity were found on the map so the peak at 0,1/2,0 (relative height 578) was attributed to the Cu-Cu vector. The surplus electron density of this peak was thought to be another manifestation of the pseudosymmetry mentioned previously. If we assume the space group $P\bar{1}$, then there are two possible sets of copper positions, 0,0,0 and 0,1/2,0 which are located on centres of symmetry (special positions) or 0,1/4,0 and 0,3/4,0 which are related by centres of symmetry (general positions).

At this stage it was not possible to distinguish between these two possibilities. Two chelate rings could be defined about each copper atom by considering additional Patterson peaks. However, there were three choices for the coordination geometry. These are depicted schematically below. If the copper atoms were located in special positions, then one of

Table 2. The Patterson Map

Peak Number	Peak Position u	v	w	Relative Height (origin set to 1000)
1	0.00	0.00	0.02	999
2	0.00	0.48	-0.02	578
3	0.10	0.44	0.14	170
4	-0.10	0.08	-0.10	169
5	-0.40	0.44	0.18	163
6	0.40	0.52	-0.18	157
7	-0.10	0.08	0.14	153
8	0.10	0.40	-0.14	140
9	-0.10	0.52	-0.14	136
10	0.40	0.04	-0.18	129
11	0.20	0.52	0.14	128
12	-0.10	0.40	-0.14	127
13	0.20	0.52	-0.14	121
14	0.25	0.00	-0.02	118
15	0.25	0.52	0.02	114
16	0.00	0.52	0.30	112
17	-0.40	0.00	0.18	110
18	-0.10	0.40	0.14	108
19	0.10	0.00	0.14	102
20	0.45	0.04	0.34	101



SQUARE PLANE (X- TILT) SQUARE PLANE (Z- TILT) FLATTENED TETRAHEDRON

the square planar geometries would be present although not necessarily the same one for both positions. On the other hand, if general positions were occupied, the two geometries would be related by a centre of symmetry but any of the three possibilities could be present.

In an effort to find the correct structure, least squares refinement and subsequent Fourier synthesis was attempted for several trial structures. The contributions to the structure factors were calculated by:

$$F(hk\ell) = \Sigma f_j \cos 2\pi (hx_j + ky_j + \ell z_j) \exp -[B_j (\sin \theta/\lambda)^2] \quad (8)$$

where x_j, y_j, z_j are the fractional coordinates, f_j is the scattering factor and B_j is the isotropic thermal parameter of the j-th atom. The wavelength of the radiation and the Bragg angle of the $hk\ell$ reflection are respectively λ and θ. Ibers and Corfield's version of Busing, Martin and Levy's ORFLS (51) programme was used for the least squares refinement. The computations were performed by a Burroughs 5500 computer. During the refinements, the function that was minimized was $\Sigma w\Delta^2$ where the weight factor is:

$$w = 1/\sigma^2 (F) \quad (9)$$

and $$\Delta = ||F_0| - |F_c|| \quad (10)$$

The correctness of a structure is usually expressed in terms of weighted (R_2) and unweighted (R_1) residual factors defined as:

$$R_1 = \Sigma\Delta/\Sigma|F_0| \quad (11)$$

$$R_2 = \Sigma w\Delta^2/\Sigma w\ F_0^2 \quad (12)$$

For the trial refinements, the overall temperature factor was set to 3.5 $\mathring{A}^2$ and all the ligands were treated as nitrogen atoms.

Fourier syntheses were calculated from observed reflections by:

$$\rho(x,y,z) = \Sigma\Sigma\Sigma F(hk\ell) \cos 2\pi (hx + ky + \ell z) \quad (13)$$

using a local version of Zalkin's FORDAP (52). In equation (13), $\rho(x,y,z)$ is the electron density at the point x,y,z in the unit cell and $F(hk\ell)$ is the observed value of the structure factor of the $hk\ell$ reflection. Difference Fourier syntheses were computed by subtracting the contributions of the trial atomic positions from the overall electron density Fourier synthesis. Normally, it is possible to determine additional atomic positions from a difference map and thereby solve the complete structure. However, in this case, it was not possible to unequivocally define the coordination geometries nor the positions of the copper atoms. In fact, during these many trial refinements, the R-factor was never less than 37% which indicated that the actual structure had not been found.

At this point, it was decided to try direct methods as a technique for solving the structure.

B. Direct Methods

The first attempt at a direct methods solution was made using the X-RAY SYSTEM of crystallographic programmes (53). Implementation of this system on the Burroughs 5500 computer was difficult and only three preliminary programmes were successfully made operational. One of these programmes, NORMSF, produced a list of normalized structure factors or E values defined by:

$$|E(hk\ell)| = |F(hk\ell)|/(\varepsilon\Sigma f_j^2)^{\frac{1}{2}} \qquad (14)$$

where ε is a symmetry related integer equal to one for a triclinic crystal (54). Since the distribution of E values is theoretically and empirically dependent on the presence or absence of a centre of symmetry, it was possible to define the space group as $P\bar{1}$. The list of values on which this conclusion was based are presented in Table 3.

In addition, a sharpened Patterson function was calculated. Previous conclusions were confirmed but no new information was obtained. Further work with the X-RAY SYSTEM was suspended when Sheldrick's SHELX (55) programme became available.

Unfortunately, attempts to produce a decipherable E map using SHELX were equally unsuccessful. It was not known whether the problem was due to the structure or to the programme itself since test runs with data from another structure determination (56) failed to duplicate known results. At one point, the signs of 170 E values greater than 1.2 were determined by hand. However, this set did not include any reflections with odd k indicating that the problems of the pseudosymmetry would not be solved in this manner.

The crystal data were almost discarded as being insoluble when, to further test the programme, a sharpened Patterson map was calculated.

Table 3. Distribution of E Values from NORMSF (X-RAY SYSTEM)

	Theoretical		Empirical
	Centric	Acentric	
Average Value of			
$\|E\|$	0.798	0.886	0.797
$\|E^2\|$	1.00	1.00	1.00
$\|E^2 - 1\|$	0.968	0.736	0.953
$\|E^2 - 1\|^2$	2.000	1.000	1.965
$\|E^2 - 1\|^3$	8.000	2.000	9.950
Number of Reflections			
With			
$\|E\| > 1.0$	31.73%	36.79%	33.99%
$\|E\| > 2.0$	4.55%	1.83%	3.93%
$\|E\| > 2.5$	1.24%	0.19%	1.09%
$\|E\| > 3.0$	0.27%	0.01%	0.20%

The results were found to agree with the map obtained from a parallel run with the X-RAY SYSTEM (53). A closer examination of this map led to the eventual solution of the structure.

C. The Sharpened Patterson Map.

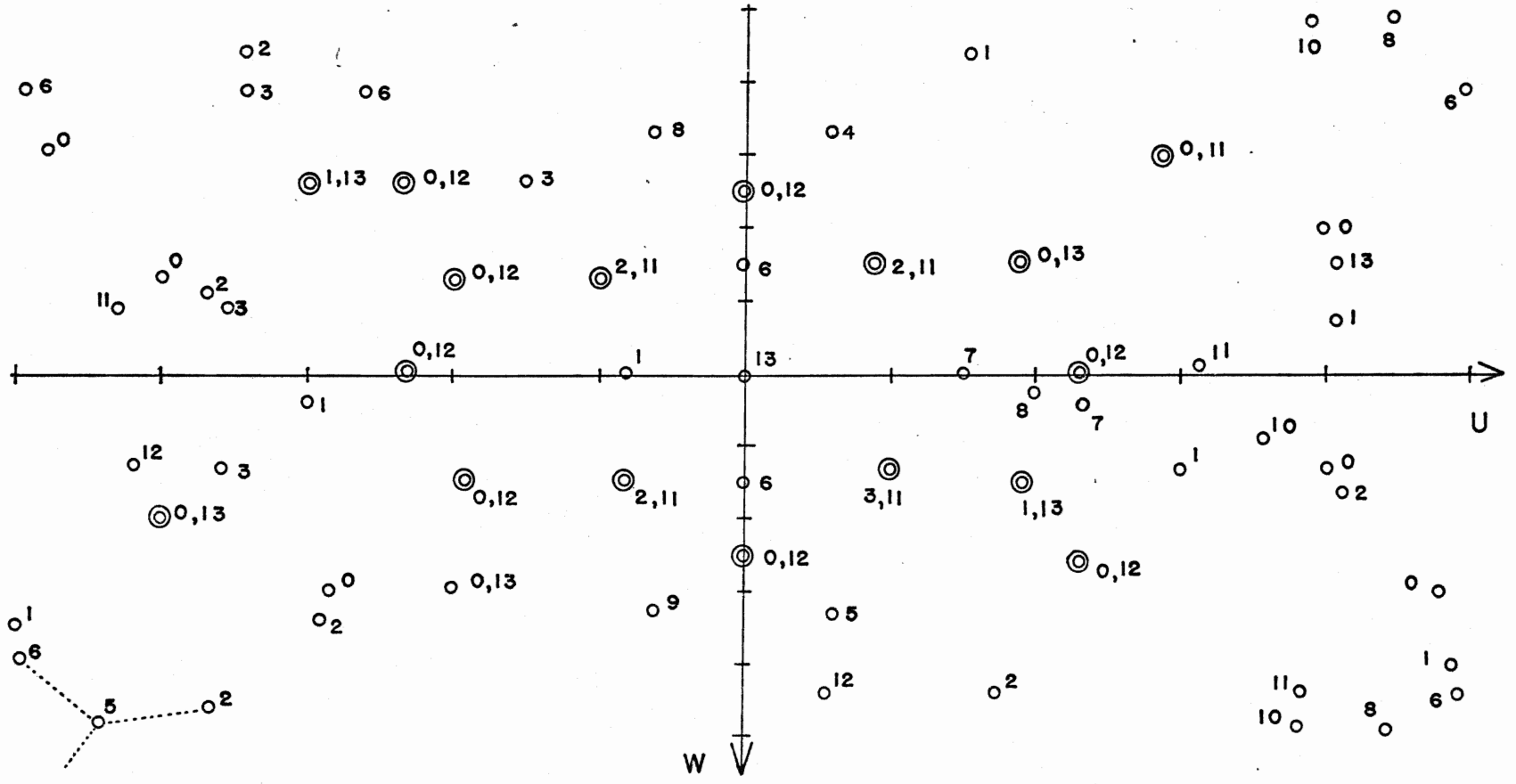
The only major technique of structure determination which had not been applied to the data was Patterson superposition. With the thought of trying this technique by hand, the complete Sharpened Patterson map was plotted and is shown in Figure 5. This map was very similar to earlier difference Fourier maps in that the presence of the chelate rings was obvious but exact geometry and further structural features were hard to define.

However, a nitrate group appeared to be present at u = -1/2, v = 1/2, w = 1/2. A trial refinement was attempted with the copper atoms in the special positions and a nitrate group centred on 0.44, 0.31, 0.52. The R-factor dropped an expected 8.5% but more importantly, a second nitrate group centred at 0, 1/4, 1/4 became fully resolved on the difference Fourier map. The presence of this bridging nitrate group confirmed the location of copper atoms in the special positions and served to break the pseudo-symmetry.

In order to define the origin consistently, the first nitrate group was ignored and the bridging nitrate group refined isotropically. Again the R-factor dropped 8.5% but this time structural features were better resolved. In the next stage, both nitrate groups plus two independent chelate rings were refined. The R-factor dropped to below 40% and from the difference map, the positions of all non-hydrogen atoms could be assigned except for one of the hydroxymethyl oxygens. The correctness of these positions was supported by a dramatic drop in the R-factor to 14.77%. The

FIGURE 5. PLOT OF SHARPENED PATTERSON PEAKS

(FRACTIONAL V COORDINATES ARE IN 26 THS)



oxygen atom in question was thought to be disordered and in later stages, site occupation factors as well as positional parameters were refined.

D. Structure Refinement

Following the location of all non-hydrogen atoms, the data set was expanded to include reflections with 2θ less than 45°. With the complete data set, thermal parameters were converted from isotropic to anisotropic and refined. A subsequent difference map revealed all the hydrogen positions. The isotropic temperature factors for hydrogen atoms were fixed at a value 20% greater than the thermal parameter of the atom to which it was bonded. A refinement of the hydrogen atom positions reduced the R-factor to below 7%.

The final cycles of refinement were postponed while a number of reflections with large $F_0 - F_c$ values were remeasured. At the same time, SHELX (55) was updated and adapted to the Burroughs 6700 computer. In testing the capacities of the new computer and revised SHELX (55) programme, isotropic temperature factors were refined for hydrogen atoms. As expected, the results were unreasonable in their magnitude but assuming that the direction of the change was real, an average value was calculated by $(2a + b)/3$ where a is the original value and b is the refined value. In addition, temperature factors were averaged and fixed for similar groups in the two independent molecules. The methyl protons were refined as rigid tetrahedral groups with C-H bond lengths fixed at 1.080 Å.

Refinement of the structure continued until the average parameter shift was less than 0.35 estimated standard deviations. In the last cycle, a

total of 397 variables were refined. For the 2390 independent reflections with $F \geq 3\sigma(F)$, the final R values were $R_1 = 0.0408$ and $R_2 = 0.0431$. A final difference map was calculated and no peaks nor holes with magnitudes greater than 0.4 electrons Å^{-3} were observed. The values of positional and thermal parameters are presented in Tables 4, 5 and 6. Observed and calculated structure factors for all the data are tabulated in Appendix A.

In the final stages of the refinement, the structure factors were weighted according to:

$$w = k/(\sigma^2(F) + |g|F^2) \qquad (15)$$

where k was determined from refined values of g. The final values were $g = 0.001062$ and $k = 1.6762$. The overall scale factor refined to 1.699 (± 0.003). The consistency of this weighting scheme was evaluated by an analysis-of-variance technique outlined in Appendix B.

Table 4. Positional Parameters of Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses

	x/a	y/b	z/c	x 10^4
Cu(1)*	0	0	0	
Cu(2)*	0	5000	0	
N(1)	2912(2)	-440(4)	-3162(4)	
C(1)	2112(3)	152(5)	-2944(4)	
C(2)	1610(4)	622(7)	-4235(5)	
C(3)	1770(3)	350(5)	-1541(4)	
O(1)	981(2)	931(3)	-1336(3)	
C(4)	2301(3)	80(4)	411(4)	
C(5)	1959(3)	223(6)	1097(5)	
N(2)	972(2)	591(4)	1297(4)	
C(6)	3136(3)	-705(5)	-702(5)	
C(7)	3740(4)	-1195(7)	481(6)	
O(2A)†	4522(4)	-1903(7)	-155(8)	
O(2B)†	4077(6)	65(11)	1546(8)	
C(8)	3430(3)	-873(5)	-2102(5)	
N(3)	3061(3)	4585(5)	2682(4)	
C(9)	2256(3)	5199(5)	2666(4)	
C(10)	1829(4)	5677(7)	4065(5)	
C(11)	1842(3)	5336(5)	1320(4)	
O(3)	1054(2)	5979(3)	1292(3)	
C(12)	2310(3)	4909(5)	75(4)	
C(13)	1866(3)	5132(6)	-1365(5)	
N(4)	877(3)	4278(4)	-1464(4)	
C(14)	3160(3)	4311(5)	164(5)	
C(15)	3622(3)	3907(6)	-1146(5)	
O(4)	4067(2)	5346(4)	-1790(4)	
C(16)	3528(3)	4168(6)	1482(5)	
N(5)	22(3)	2613(4)	2751(4)	
O(5)	9(2)	2554(3)	1402(3)	
O(6)	567(3)	1900(4)	3385(4)	
O(7)	-513(3)	3373(4)	3445(3)	
N(6)	4480(4)	3118(5)	5116(5)	
O(8)	4933(3)	2844(6)	6177(4)	
O(9)	4618(4)	2539(5)	3908(4)	
O(10)	3880(3)	4031(5)	5312(4)	
O(11)	3697(3)	-879(6)	4195(4)	

* Positions fixed by symmetry

† Disordered atoms: site occupation factor refined to 0.569(11) for atoms labelled A, 0.431(11) for atoms labelled B.

Table 5. Anisotropic Thermal Parameters* for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12} x 10^4
Cu(1)	276(4)	290(4)	312(4)	72(3)	32(3)	102(3)
Cu(2)	235(4)	303(4)	388(4)	-28(3)	4(3)	91(3)
N(1)	339(21)	509(23)	345(21)	38(18)	97(17)	122(18)
C(1)	326(25)	386(25)	380(25)	47(20)	24(19)	60(20)
C(2)	557(32)	826(39)	353(28)	200(26)	23(23)	264(28)
C(3)	299(23)	265(21)	346(24)	27(18)	58(18)	81(18)
O(1)	342(16)	294(15)	391(17)	116(13)	50(13)	136(13)
C(4)	243(21)	263(21)	347(23)	19(18)	4(17)	26(17)
C(5)	306(24)	421(27)	323(25)	-31(20)	-26(18)	56(20)
N(2)	334(20)	294(19)	302(20)	24(16)	39(16)	91(16)
C(6)	268(23)	281(23)	451(28)	46(20)	-14(20)	25(18)
C(7)	289(28)	460(35)	481(32)	53(25)	-59(24)	67(25)
O(2A)	330(35)	480(38)	502(44)	47(29)	-23(26)	124(28)
O(2B)	393(49)	577(56)	355(45)	64(42)	-91(38)	-51(38)
C(8)	295(24)	472(28)	431(28)	-16(21)	38(20)	148(21)
N(3)	314(22)	583(26)	325(23)	35(20)	-37(17)	86(19)
C(9)	281(24)	475(27)	315(26)	-17(20)	16(19)	40(21)
C(10)	505(32)	710(36)	410(30)	-71(26)	9(24)	155(27)
C(11)	242(23)	283(23)	375(26)	9(19)	9(19)	59(18)
O(3)	254(16)	340(16)	439(18)	-54(13)	10(13)	98(13)
C(12)	253(23)	300(23)	329(25)	37(19)	13(18)	5(18)
C(13)	246(24)	374(26)	384(26)	73(21)	-11(19)	38(20)
N(4)	249(20)	292(20)	337(21)	43(17)	-32(16)	58(16)
C(14)	242(24)	392(26)	376(29)	72(21)	8(20)	59(20)
C(15)	312(26)	498(30)	366(26)	26(22)	74(20)	132(22)
O(4)	470(20)	560(22)	406(19)	27(17)	156(16)	50(16)
C(16)	285(25)	566(32)	407(29)	32(23)	0(21)	190(23)
N(5)	461(23)	372(21)	354(23)	40(18)	1(18)	143(18)
O(5)	685(22)	363(17)	285(18)	19(13)	-4(15)	142(15)
O(6)	907(27)	643(23)	484(20)	-89(17)	-247(19)	498(21)
O(7)	822(26)	757(24)	422(19)	128(17)	210(18)	507(22)
N(6)	797(34)	607(29)	386(28)	52(22)	2(24)	153(26)
O(8)	1250(39)	1324(42)	440(25)	52(24)	-43(24)	802(34)
O(9)	1553(46)	915(33)	369(24)	-59(22)	122(25)	498(31)
O(10)	760(28)	1053(33)	440(22)	27(21)	-39(19)	437(26)
O(11)	732(28)	877(32)	508(23)	79(21)	236(20)	293(23)

* Anisotropic temperature factors are given by:

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{12}hka^*b^*\cos\gamma^* + 2U_{13}h\ell a^*c^*\cos\beta^* + 2U_{23}k\ell b^*c^*\cos\alpha^*)]$$

where U_{ij} are thermal parameters expressed in terms of mean-square amplitudes of vibration in Angstroms.

Table 6. Positional and Isotropic Thermal Parameters for Hydrogen Atoms with Estimated Standard Deviations in Parentheses.

Part A. The following hydrogen atoms were located on a difference Fourier map. Refinement of these positions followed standard procedures.

	x/a	y/b	z/c	$10U^{\dagger} \times 10^3$
H(1)	321(3)	-48(6)	-401(5)	566
H(5)	199(3)	140(5)	133(4)	334
H(6)	236(3)	-14(5)	179(4)	334
H(7)	100(4)	-159(6)	130(5)	652
H(8)	83(4)	27(6)	209(6)	652
H(12)	397(3)	-135(5)	-238(4)	394
H(13)	331(4)	446(7)	354(6)	715
H(17)	188(3)	625(5)	-139(4)	334
H(18)	232(3)	468(5)	-209(4)	334
H(19)	62(4)	443(7)	-233(6)	652
H(20)	83(4)	326(6)	-149(5)	652
H(21)	331(4)	314(6)	-182(6)	663
H(22)	426(4)	335(6)	-90(5)	663
H(23)	422(4)	520(6)	-266(6)	597
H(24)	409(3)	377(5)	160(4)	394
H(25)	416(4)	-143(7)	418(6)	738
H(26)	393(4)	-7(7)	381(6)	738

Part B. The following hydrogen atoms constitute two methyl groups. In both cases, the H-C bond length was fixed at 1.080 Å and the H-C-H bond angles at 109.5°. The resulting rigid group was refined with respect to rotation about the carbon-carbon bonds (i.e., C(1)-C(2) and C(9)-C(10)).

	x/a	y/b	z/c	$U^{\dagger} \times 10^4$
H(2)	983(4)	1143(7)	-3971(5)	946
H(3)	1415(4)	-443(7)	-4930(5)	946
H(4)	2113(4)	1445(7)	-4778(5)	946
H(14)	1206(4)	6220(7)	3918(5)	946
H(15)	2357(4)	6500(7)	4678(5)	946
H(16)	1639(4)	4620(7)	4636(5)	946

Table 6. (continued)

Part C. The following hydrogen atoms were part of a disordered hydroxymethyl group attached to the PM molecule associated with Cu(1). Site occupation factors refined to 0.569(11) for atoms labelled A and 0.431(11) for atoms labelled B. Positions for H(9) and H(10) were calculated on the basis of the geometry of an hydroxymethyl group. The H(11) atoms were visible on the difference Fourier map and were otherwise refined according to standard procedures.

	x/a	y/b	z/c	10U† x 10^3
H(9A)	340(3)	-187(5)	115(5)	663
H(9B)	309(3)	-196(6)	122(4)	663
H(10A)	406(3)	-12(4)	103(5)	663
H(10B)	430(4)	-178(7)	19(6)	663
H(11A)	433(7)	-265(11)	73(10)	597
H(11B)	462(9)	67(15)	128(13)	597

† Isotropic temperature factors are given by $\exp[-8\pi^2 U \sin^2 \theta/\lambda^2]$.

Chapter IV

Discussion and Results

The overall structure of $Cu(PM)_2(NO_3)_2 \cdot H_2O$ is shown in Figure 6. The view depicted is a projection onto the xy plane followed by a 20° rotation about y to avoid overlap. Cu(1) lies at the origin (0, 0, 0) and Cu(2) at (0, ½, 0) with both atoms located on centres of symmetry. The pseudo-symmetry due to these copper positions is reinforced by the fact that many of the remaining atoms are also half a unit cell apart in the y-direction.

Each copper atom is chelated by two centrosymmetrically related PM molecules through the amino groups and deprotonated phenolate oxygen atoms. The presence of zwitterion III (see Figure 4) was further confirmed by the location of protons H(1) and H(19) on the two heterocyclic nitrogen atoms. The two independent $Cu(PM)_2$ moieties are symmetrically bridged by a single oxygen atom from one of the nitrate groups. The second nitrate group is not coordinated to the copper atoms but is central to an extensive hydrogen bonding network involving the water molecule and uncoordinated functional groups of PM. These aspects are discussed in greater detail in the following sections.

A. The Pyridoxamine Molecules

The bond lengths and angles together with their estimated standard deviations for the two independent pairs of PM molecules are shown in Figures 7 and 8. Angles involving hydrogen atoms are presented in Table 7. From this information, the existence of PM in the zwitterionic form III

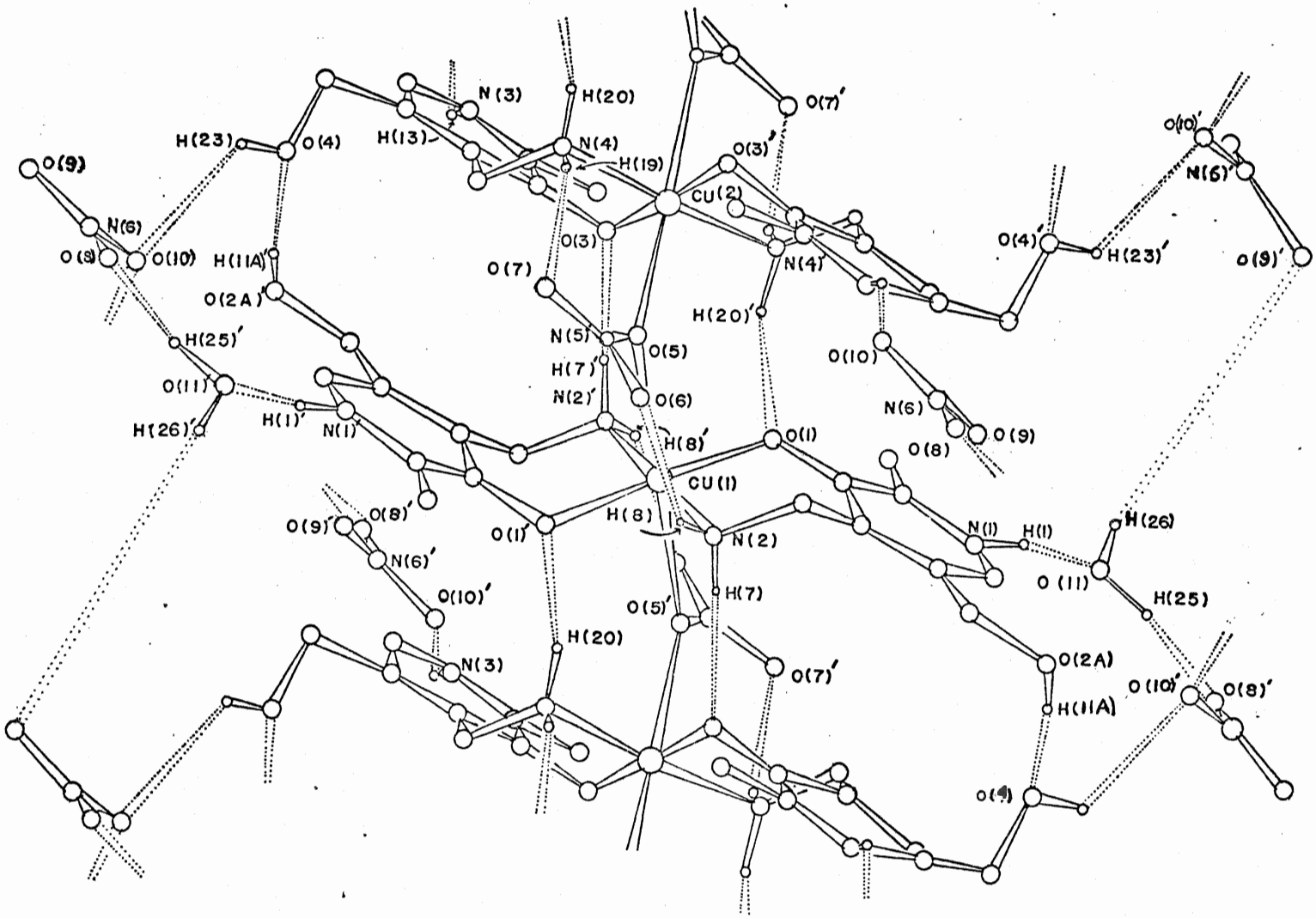
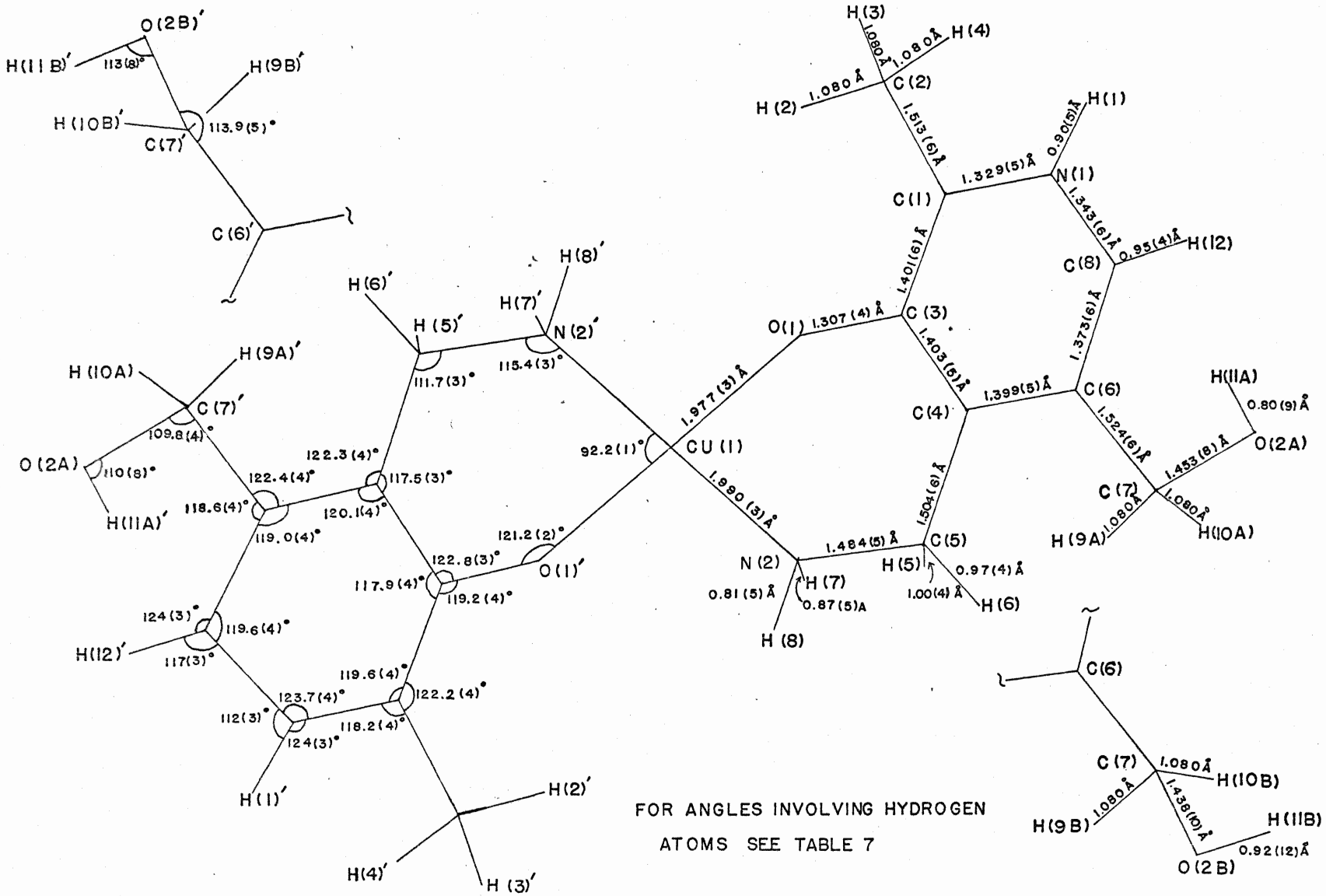


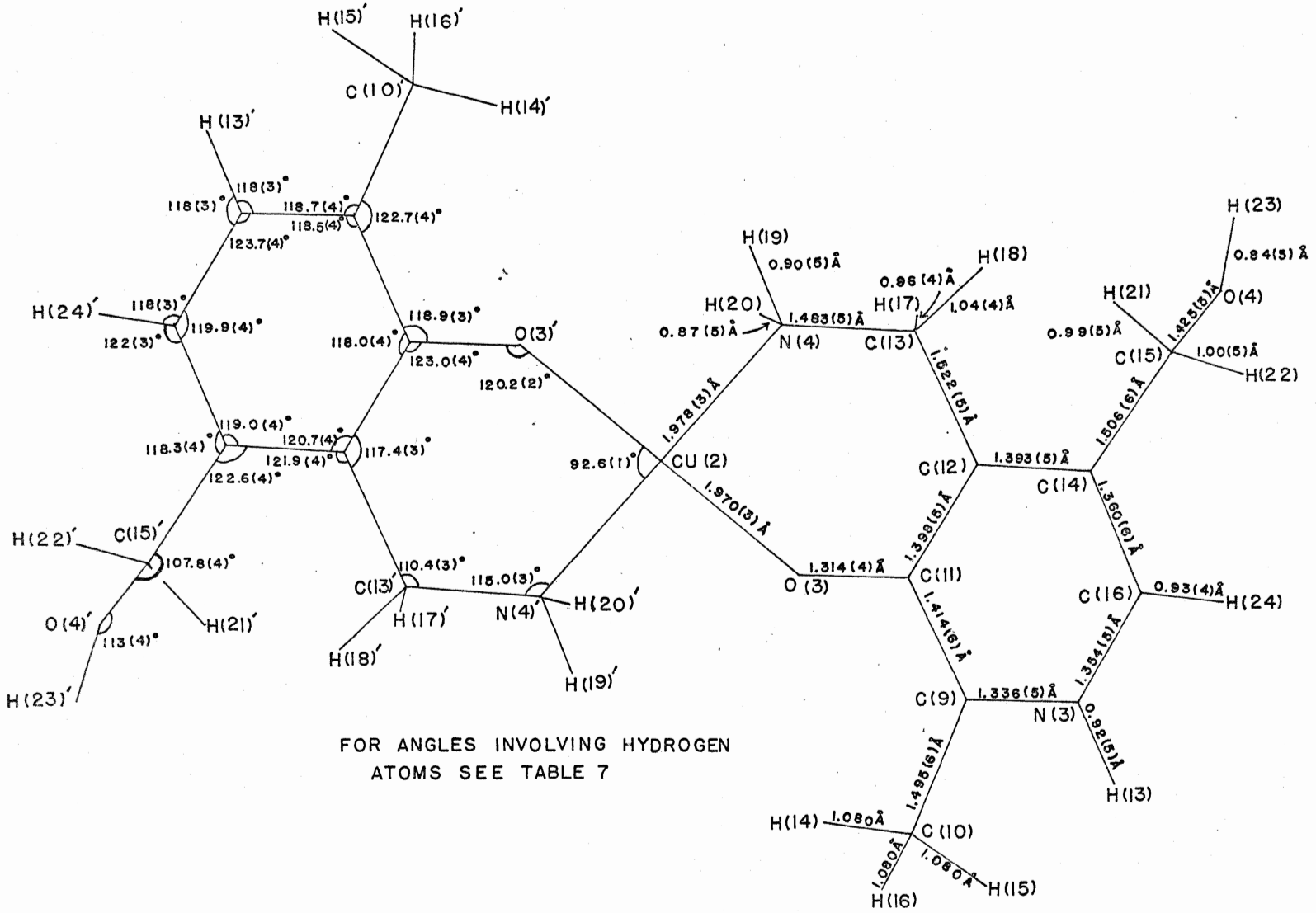
FIGURE 6. THE STRUCTURE OF $CU(PM)_2(NO_3)_2 \cdot H_2O$

FIGURE 7. DISTANCES AND ANGLES IN PYRIDOXAMINE COORDINATED TO COPPER ATOM ONE



FOR ANGLES INVOLVING HYDROGEN ATOMS SEE TABLE 7

FIGURE 8. DISTANCES AND ANGLES IN PYRIDOXAMINE COORDINATED TO COPPER ATOM TWO



FOR ANGLES INVOLVING HYDROGEN ATOMS SEE TABLE 7

Table 7. Angles Involving Hydrogen Atoms with Estimated Standard Deviations in Parentheses.

H(1)-N(1)-C(1)	124(3)°	H(8)-N(2)-C(5)	104(4)°
H(1)-N(1)-C(8)	112(3)°	H(8)-N(2)-Cu(1)	105(4)°
H(2)-C(2)-C(1)	114.1(2)°	H(9A)-C(7)-C(6)	115(4)°
*H(2)-C(2)-H(3)	109.5°	H(9A)-C(7)-O(2A)	111(4)°
*H(2)-C(2)-H(4)	109.5°	H(9A)-C(7)-H(10A)	110(5)°
*H(3)-C(2)-C(1)	106.7(3)°	H(10A)-C(7)-C(6)	105(4)°
*H(3)-C(2)-H(4)	109.5°	H(10A)-C(7)-O(2A)	105(4)°
*H(4)-C(2)-C(1)	107.6(3)°	H(11A)-O(2A)-C(7)	110(7)°
H(5)-C(5)-C(4)	110(2)°	H(9B)-C(7)-C(6)	100(4)°
H(5)-C(5)-N(2)	110(2)°	H(9B)-C(7)-O(2B)	98(4)°
H(5)-C(5)-H(6)	107(3)°	H(9B)-C(7)-H(10B)	116(6)°
H(6)-C(5)-C(4)	111(2)°	H(10B)-C(7)-C(6)	118(4)°
H(6)-C(5)-N(2)	108(2)°	H(10B)-C(7)-O(2B)	108(4)°
H(7)-N(2)-C(5)	107(3)°	H(11B)-O(2B)-C(7)	113(8)°
H(7)-N(2)-Cu(1)	116(3)°	H(12)-C(8)-C(6)	124(2)°
H(7)-N(2)-H(8)	108(5)°	H(12)-C(8)-N(1)	117(2)°
H(13)-N(3)-C(9)	118(3)°	H(19)-N(14)-Cu(2)	109(3)°
H(13)-N(3)-C(16)	118(3)°	H(19)-N(4)-H(20)	102(4)°
*H(14)-C(10)-C(9)	111.6(2)°	H(20)-H(4)-C(13)	114(3)°
*H(14)-C(10)-H(15)	109.5°	H(20)-N(4)-Cu(2)	109(3)°
*H(14)-C(10)-H(16)	109.5°	H(21)-C(15)-C(14)	110(3)°
*H(15)-C(10)-C(9)	108.9(2)°	H(21)-C(15)-O(4)	112(3)°
*H(15)-C(10)-H(16)	109.5°	H(21)-C(15)-H(22)	105(4)°
*H(16)-C(10)-C(9)	107.9(3)°	H(22)-C(15)-C(14)	111(3)°
H(17)-C(13)-C(12)	105(2)°	H(22)-C(15)-O(4)	111(3)°
H(17)-C(13)-N(4)	110(2)°	H(23)-O(4)-C(15)	113(4)°
H(17)-C(13)-H(18)	115(3)°	H(24)-C(16)-C(14)	122(2)°
H(18)-C(13)-C(12)	102(2)°	H(24)-C(16)-N(3)	118(2)°
H(18)-C(13)-N(4)	114(2)°	H(25)-O(11)-H(26)	104(5)°
H(19)-N(4)-C(13)	107(3)°		

* Methyl protons refined as a rigid group (see Table 6, Part B).

(see Figure 4) can be quickly established. First of all, protons H(1) and H(13) are located on the heterocyclic nitrogen atoms, N(1) and N(3) respectively. Both of these protons were easily found on a difference Fourier map. Secondly, no protons could be located in the region of the two phenolate oxygen atoms.

Both pyridine skeletons are planar within experimental error. For the PM molecule coordinated to Cu(1), the equation of the mean plane is:

$$0.5237\ X + 0.8468\ Y + 0.0930\ Z = 1.18119$$

while the equation for the PM molecule associated with Cu(2) is:

$$0.5160\ X + 0.8566\ Y - 0.0056\ Z = 4.8332$$

The perpendicular distances to these planes for the atoms defining the plane and for substituents on the pyridine rings are presented in Table 8. The average C-C bond length in the ring is 1.393 Å. No explanation for significant deviations from this average value (e.g., C(14)-C(16), 1,360(6) Å; C(9)-C(11), 1.414(6) Å) is offered since there appears to be no consistent correlation with possible resonance structures (see Figure 9). However, differences of similar magnitude have been reported in accurate structure determinations of other pyridine-containing compounds (57, and references cited therein). The average C-N bond length is 1.340 Å. The six $C(sp^2)$-$C(sp^3)$ bond lengths have a mean value of 1.511 Å. Each of the average values is within the standard range cited for the respective bond types (58).

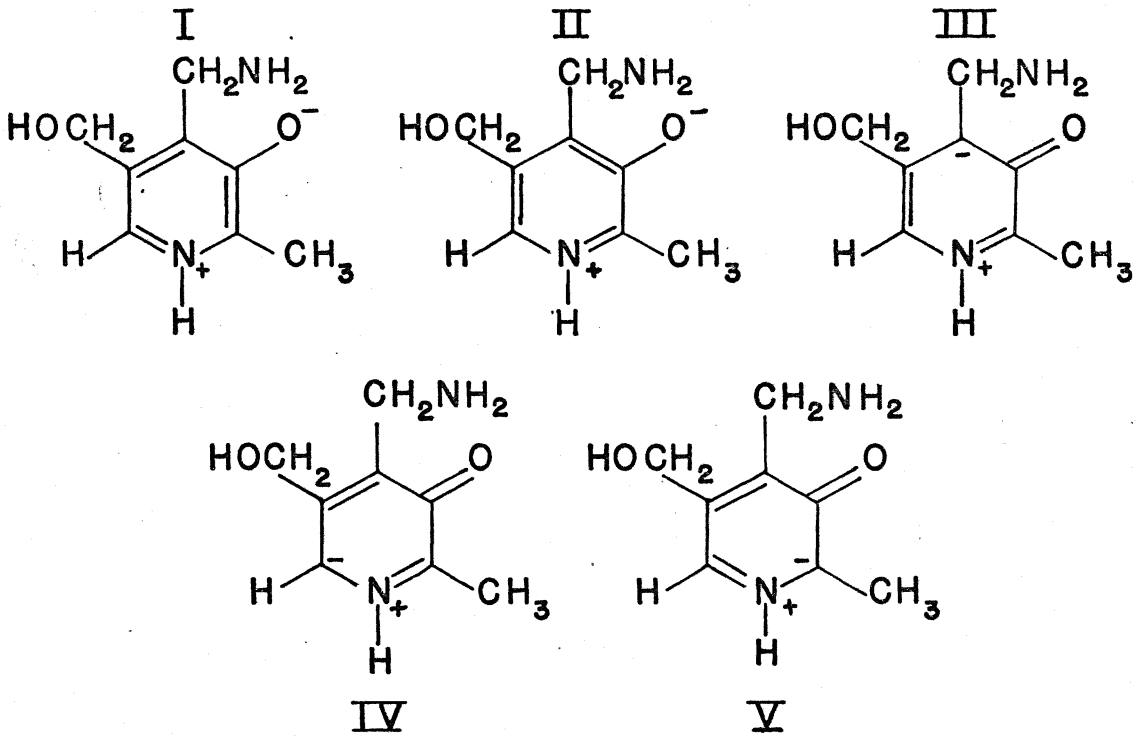
As a result of protonation, the valence angles at the heterocyclic nitrogen atoms have been distorted. The values of 123.7° and 123.8° for N(1) and N(3) respectively are in good agreement with the observations of Singh (59). In a survey of the literature, he found that protonated nitrogen atoms in six-membered heterocycles had angles in the range of 125 ± 3° while unprotonated species had angles in the range of 116 ± 3°. This

Table 8. Deviations of Atoms from Least-Squares Planes (in Å)

Cu(1)-PM		Cu(2)-PM	
N(1)*	0.0017	N(3)*	0.0132
H(1)	0.1121	H(13)	0.0254
C(1)*	0.0009	C(9)*	-0.0094
C(2)	0.0332	C(10)	-0.0402
C(3)*	-0.0039	C(11)*	-0.0006
O(1)	-0.0070	O(3)	-0.0309
C(4)*	0.0043	C(12)*	0.0058
C(5)	0.0785	C(13)	-0.0154
C(6)*	-0.0018	C(14)*	-0.0026
C(7)	0.0041	C(15)	-0.0899
C(8)*	-0.0013	C(16)*	-0.00684
H(12)	-0.0602	H(24)	-0.0045

* Atoms defining the plane.

FIGURE 9. RESONANCE STRUCTURES



phenomenon has also been observed in crystal structures of other compounds related to vitamin B_6 and can be used to determine protonation sites although the protons themselves were not necessarily located (31,60-63).

Another structural feature of interest involves the phenolate oxygen atoms. The bond lengths of 1.307 and 1.314 Å for C(3)-O(1) and C(11)-O(3) respectively are similar to the values of 1.28 and 1.30 Å which were found in a metal-Schiff base complex where the phenolate oxygen was coordinated to Ni(II) (31). In contrast to these values are the somewhat longer distances of 1.34 to 1.35 Å recorded for structures in which the phenolate oxygen atom was protonated (60-63). An explanation for this difference can be found by considering the resonance forms shown in Figure 9. From the short C-O bond lengths and valence angles of approximately 120° observed in this structure and in the Ni(II) Schiff base complex (31), it would appear that forms III, IV and V make significant contributions to the observed structures where the phenolate oxygen atoms are deprotonated. On the other hand, similar resonance structures, VII, IX and X, for protonated phenolate groups would involve the location of an unstable positive formal charge on the oxygen atom. Therefore, such forms would be expected to make relatively small contributions to the overall structure, resulting in a longer C-O bond.

B. Copper Coordination

The two independent copper atoms are located at centres of symmetry at (0, 0, 0) and (0, ½, 0). The coordinated ligands define a tetragonally distorted octahedron. Distances are shown in Figure 10 and relevant angles are presented in Table 9. The amino nitrogen atom, N(2), and the phenolate oxygen atom, O(1), from one PM molecule together with the correspond-

FIGURE 10. THE COPPER COORDINATION SPHERE

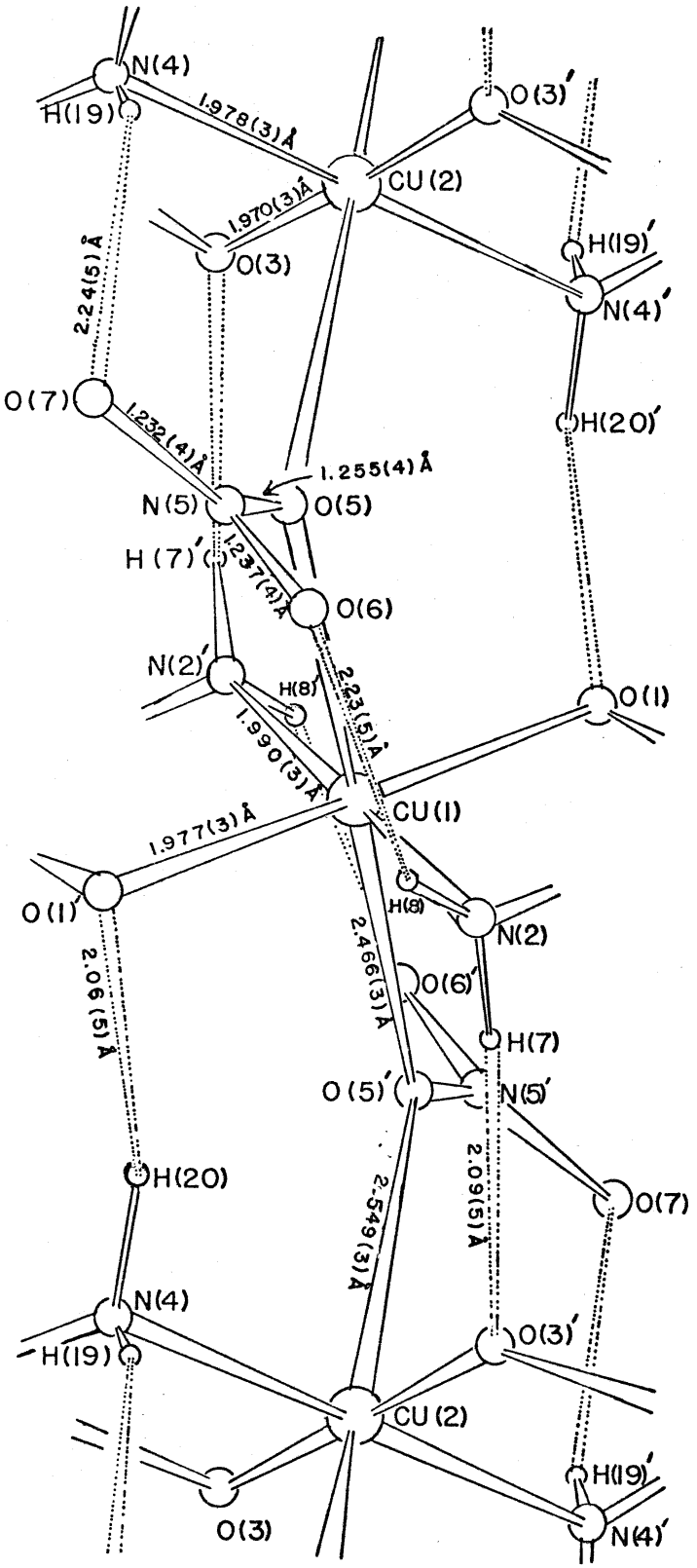


Table 9. Some Distances, Angles and Planes Associated with Figure 10.

O(1)-Cu(1)-N(2)	92.2°	O(5)-N(5)-O(6)	120.1°
O(1)-Cu(1)-N(2)'	87.8°	O(5)-N(5)-O(7)	119.9°
I(1)-Cu(1)-O(5)	92.6°	O(6)-N(5)-O(7)	119.9°
N(2)-Cu(1)-O(5)	91.4°	N(2)-H(8)...O(6)	143°
O(3)-Cu(2)-N(4)	92.6°	N(5)-O(6)...H(8)	111°
O(3)-Cu(2)-N(4)'	87.4°	N(2)-H(7)...O(3)'	180°
O(3)-Cu(2)-O(5)	84.9°	Cu(2)-O(3)'...H(7)	104°
H(4)-Cu(2)-O(5)	92.2°	N(4)-H(20)...O(1)'	169°
Cu(1)-O(5)-Cu(2)	117.3°	Cu(1)-O(1)'...H(20)	108°
Cu(1)-O(5)-N(5)	120.0°	N(4)-H(19)...O(7)	132°
Cu(2)-O(5)-N(5)	122.7°	N(5)-O(7)...H(19)	109°

The equation of the plane defined by the nitrate group is:

$$0.7033\ X + 0.7106\ Y + 0.0206\ Z = 1.5179$$

The equation of the plane defined by Cu(1)-O(5)-Cu(2) is:

$$1.0000\ X + 0.0000\ Y - 0.0030\ Z = 0.0000$$

The dihedral angle between the above planes is 45.3°.

Additional Distances

O(1)-N(2)	2.858 Å	O(3)-N(4)	2.853 Å
O(1)-N(2)'	2.752 Å	O(3)-N(4)'	2.729 Å

Deviations of Atoms from Least-Squares Planes (in Å)

Cu(1) Chelate Ring		Cu(2) Chelate Ring	
Cu(1)*	0.0084	Cu(2)*	-0.0234
O(1)	0.4348	O(3)	-0.4296
C(3)*	-0.0119	C(11)*	0.0331
C(4)*	0.0133	C(12)*	-0.0370
C(5)	0.6453	C(13)	-0.6752
N(2)*	-0.0098	N(4)*	0.0272

* Atoms defining the plane

ing pair of atoms from the centrosymmetrically related PM molecule define a slightly distorted square plane at Cu(1). A similar but independent square plane is defined at Cu(2) by N(4) and O(3). The intrachelate N-Cu-O angles, 92.2° and 92.9° respectively, are very close to the ideal value of 90°. The distortion from a perfect square is also marked by a difference of 0.1 Å between the N-O and N-O' separations (see Table 9). These variations can be attributed to the difference in ligands and the constraints of the six-membered chelate rings. Metal-ligand bond lengths are similar to values found in other structures (64).

The octahedral sites of both copper atoms are occupied by a single nitrate oxygen atom, O(5). Since the Cu-O(5) bond lengths differ from the bond lengths found in the square plane, the coordination at each copper atom may be described as (4 + 2) (64). The tetragonal distortion present here is of the type usually observed when Jahn-Teller effects are operative in octahedral complexes (64). However, the type of nitrate-oxygen bridge found in this structure is not so common. Only three other examples of this type of bridging nitrate group could be found in the literature: α-$Cu(NO_3)_2$ (65), $[Cu(NO_3)_2py_2]_2py$, (py = pyridine) (66) and $[Ag\{P(OMe)_3\}_2NO_3]_2$ (67). In each case, a nonbridging oxygen atom was also coordinated to the metal atom, either strongly (2.02 Å, 65) or weakly (2.90 Å, 66; 3.01 Å, 67). The net result was that the metal ion undergoing the additional bonding is very close to the plane of the nitrate group while the second metal atom in the bridged unit is much further removed from the plane.

In the present structure, neither of the nonbridging oxygen atoms interacts with the copper atoms: the Cu(1)-O(6) and Cu(2)-O(7) distances are 3.483 and 3.616 Å respectively. Furthermore, the nitrate group is

twisted by 44.7 ° about the O(5)-N(5) bond so that the Cu(1) and Cu(2) atoms are located more than 1.51 Å from the nitrate plane, on opposite sides. This twisting of the nitrate group is quite surprizing for two reasons. First of all, the N(2)-O(5) bond length of 1.255 Å and the Cu(1)-O(5)-Cu(2) bond angle of 117.3° indicate that the O(5) atom is sp^2-hybridized. Thus, the copper atoms would be expected to be in the plane of the nitrate group to establish maximum overlap between the lone electron pairs from O(5) and the orbitals on Cu(1) and Cu(2). Secondly, coplanarity would minimize any steric crowding of the nitrate group by the two $Cu(PM)_2$ moieties. However, these considerations appear to have been overshadowed by the formation of two hydrogen bonds which is made possible by the twisting. The relevant distances are 2.225 Å for O(6)...H(8) and 2.243 Å for O(7)...H(19)' (see also Table 9).

A final noteworthy feature of the copper coordination is the conformation of the chelate rings. In the six-membered ring incorporating Cu(1), the metal atom, N(2), C(3) and C(4) are coplanar within experimental error while O(1) and C(5) are 0.4348 and 0.6453 Å above the plane respectively. The resulting boat conformation is distorted since two of the six bonds are considerably longer than the other four. A similar boat can be defined at Cu(2) with O(3) and N(4) being 0.4296 and 0.6752 Å below the plane (see Table 9).

Six-membered chelate rings have been found to exist in boat conformations for a series of metal complexes of 2(2-aminoethyl)pyridines (57 and references cited therein). In these compounds, the metal atom occupies one of the two "flagpole" positions which is not the case in this structure. The difference in conformations can be attributed to the formation of hydrogen bonds to the bridging nitrate (vide supra) as well as an additional inter-

action involving the phenolate and amino groups. The oxygen atoms coordinated to one copper atom are hydrogen bonded to the amino protons associated with the other metal atom (see Figure 10 and Table 9). These interactions together with the hydrogen bonds to O(6) and O(7) create a sheath surrounding the infinite chain defined by the copper atoms and the bridging nitrate group. Linkages between these columns, which are aligned in the y direction, will be described in the next section.

Although Cu(1) and Cu(2) are not related crystallographically, the chemical environments of both metal centres are very similar. This similarity extends to the surrounding hydrogen bonding network (see Figure 10). For example, the amino protons, H(19) and H(20) undergo interactions which parallel those found for H(7) and H(8) on the independent amino group. This reciprocal arrangement between independent atoms in this structure is very striking and accounts for some of the difficulty in solving the Patterson map (vide supra).

C. Molecular Packing

The dominant feature of molecular packing is the sheath of interactions surrounding the infinite chain formed by the copper atoms and bridging nitrate groups. This series of bonds and hydrogen bonds is shown in Figure 10 and fully described in the preceding section. The cross-linkage between these columns is of two types with each type associated with layers formed by each of the independent copper atoms. A brief description of each type will be followed by a discussion of the participating hydrogen bonds. A final paragraph will deal with the disordered hydroxymethyl group.

Firstly, the Cu(1) complex at (0, 0, 0) is diagonally connected to the Cu(1) complex at (1, 0, -1). The protonated heterocyclic nitrogen atoms,

N(1) and N(3)', of the PM molecules coordinated to the respective copper atoms are hydrogen bonded (see Figure 11) to two centrosymmetrically related water molecules O(11) and O(11)'. These in turn are doubly linked by a pair of (uncoordinated) nitrate groups which are related by the same centre of symmetry. The importance of this "ring-like" structure of nitrate and water molecules is described below. A schematic of this first type of intercolumn linkage is shown in Figure 12.

The second type of cross-linkage joins Cu(2) complexes related by translation in the z direction. The protonated heterocyclic nitrogen atom of one PM molecule is connected to the hydroxymethyl group of the next by means of a nitrate oxygen atom, O(10). A second interaction of this type is generated by the centre of symmetry at (0, ½, ½). The (uncoordinated) nitrate group linking Cu(2) complexes also forms the ring of interactions with the water molecules (vide supra). Thus the translational Cu(2) series is connected to the diagonal Cu(1) series. In addition, the Cu(2) string at (0, ½, z) is joined diagonally to a parallel series at (1, -½, z) through the same ring structure. Both the translational and diagonal connections involving Cu(2) complexes are illustrated in Figure 12.

The above interactions are shown in greater detail in Figure 11. The view is a projection onto the xz plane with the primed atoms related to the unprimed by a centre of symmetry at (½, 0, ½). To establish perspective in this figure, the linkage from O(4) through O(10) to N(3) is more or less in the plane of y = ½. The N(1), O(11), O(11)' and N(1)' atoms are distributed about y = 0 while the O(4)'-O(10)'-N(13)' link is at y = -½. The primed and unprimed nitrate groups are located at y = ¼ and y = -¼ respectively. Relevant distances and angles are listed in Table 10.

FIGURE II. INTERACTIONS OF UNCOORDINATED NITRATE AND WATER MOLECULES

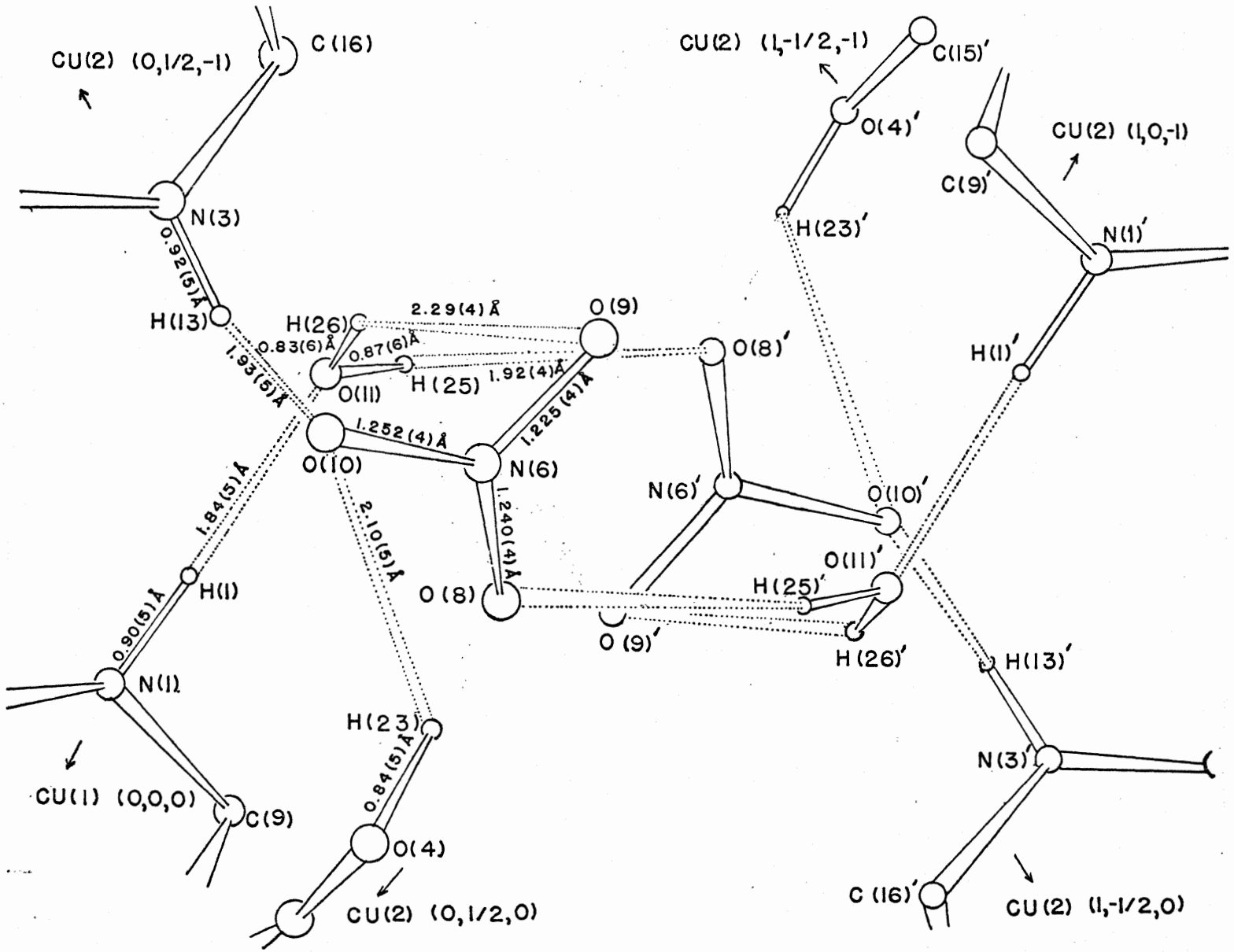


Table 10 Some Distances and Angles Associated with Figure 11.

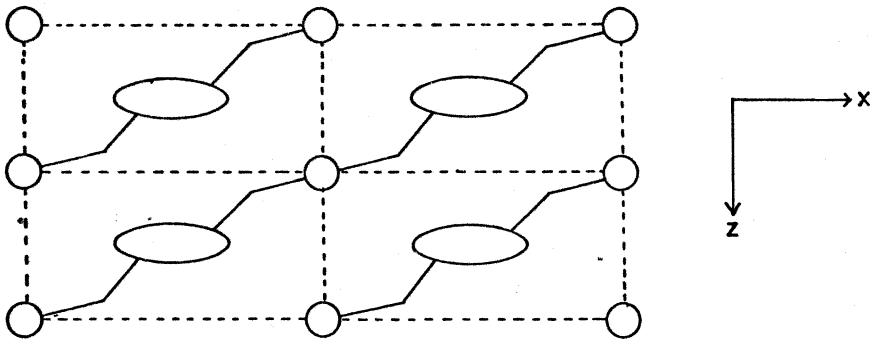
Hydrogen Bonds

A-B...C-D	<ABC	<BCD	A...C
N(1)-H(1)...O(11)-H(25)	171(3)°	115(3)°	2.727(5) Å
N(3)-H(13)...O(10)-H(6)	175(3)°	112(3)°	2.833(5) Å
O(4)-H(23)...O(10)-N(6)	148(4)°	105(4)°	2.848(5) Å
O(11)-H(25)...O(8)'-N(6)	169(5)°	116(5)°	2.778(5) Å
O(11)-H(26)...O(9)-N(6)	152(5)°	107(5)°	3.043(5) Å
O(2A)-H(11A)...O(4)-C(15)	162(7)°	124(7)°	2.706(8) Å
O(11)-H(26)...O(2B)-C(7)	124(8)°	125(8)°	2.678(10) Å

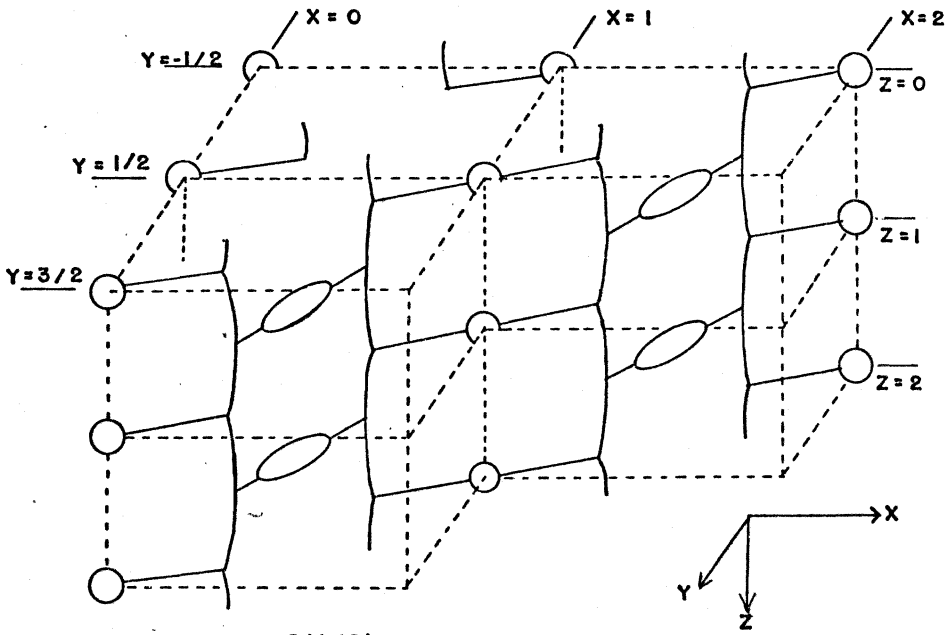
Nitrate Group and Water Molecule

O(8)-N(6)-O(9)	121.7(5)°
O(8)-N(6)-O(10)	117.7(4)°
O(9)-N(6)-O(10)	120.6(4)°
H(25)-O(11)-H(26)	104(5)°

FIGURE 12. SCHEMATIC DIAGRAMS OF INTERCOLUMN LINKAGES



CU (1) LAYERS



CU (2) LAYERS

O METAL CENTRES ------ UNIT CELL EDGES

NITRATE - WATER INTERACTIONS —— PM MOLECULES

PM MOLECULES HYDROGEN-BONDED TO WATER IN

NITRATE LINKAGES OF TWO PM MOLECULES TO

As shown in Figure 11, the primed and unprimed nitrate groups are doubly bridged by centrosymmetrically related water molecules. The hydrogen bonds involving H(25) and H(26) are within the standard range (58). The oxygen atoms of the water molecules are tightly hydrogen bonded to the protonated heterocyclic nitrogen atoms of PM molecules coordinated to Cu(1) atoms. The N(1)-O(11) separation of 2.727 Å is actually less than the sum of van der Waal's radii for nitrogen and oxygen (2.9 Å). A very short contact also characterizes the protonated nitrogen atom in the independent PM molecule (N(3)-O(10), 2.822 Å). The ability of these protonated heterocyclic nitrogen atoms to form very strong hydrogen bonds is consistent with the importance of this group in the binding of the coenzyme to the enzyme (10). The remaining contact (2.103 Å) between H(23) and O(10) is within standard values (58).

Finally, the disorder of the hydroxymethyl group attached to C(6) can be attributed to the fact that this group can participate in two different hydrogen bonds. In the most populated orientation (site occupation factor of 0.569), H(11A) is 1.935 Å away from O(4). This contact is shown in Figure 6. The second orientation involves a contact of 2.125 Å between O(2B) and H(26) and is not illustrated. The differences in the population distribution of these two orientations is probably due to the relative strengths of the hydrogen bonds which are formed in each case.

Chapter V

Conclusion

The crystal structure of a copper II complex with the pyridoxamine form of vitamin B_6 has been determined. In the complex, the metal atoms are chelated by methyl amino and deprotonated phenolate oxygen groups. The rigid square planar geometry defined by these atoms is consistent with both the inability of copper to assist in Schiff base formation (21) and the catalytic effectiveness of copper in model transamination and similar reactions (31) (vide supra). This is in contrast to natural systems where the enzyme is active in both reactions.

Also in this complex, the zwitterionic form of pyridoxamine was found to involve deprotonation of the phenolic group and protonation of the heterocyclic nitrogen atom. This form is different from that thought to be the dominant species in solution (34). However, protonation of the heterocyclic nitrogen atom is important in enzymatic systems, both as an electron sink and binding site (12). Since the former aspect is also important in model reactions, the metal ion in vitro may duplicate an enzymatic function by inducing the required zwitterionic structure through chelate formation.

Finally, the two independent copper complexes in this structure are bridged by a single nitrate oxygen atom. This bridge appears to be unique (65-67) in that neither of the nonbridging nitrate oxygen atoms interacts with a metal atom. Consequently, the formation of relatively weak hydrogen bonds has resulted in a large angle (45°) between the plane of the nitrate molecule and that defined by the copper atoms and bridging oxygen atom.

Bibliography

1. A. F. Wagner and K. Folkers, Vitamins and Coenzymes, Interscience Publishers, New York, N.Y. (1964). pp. 1-7.

2. G.M. Badger, The Chemistry of Heterocyclic Compounds, Academic Press, New York, N.Y. (1961). p. 210.

3. E. E. Snell, Compr. Biochem., 11, 48 (1963).

4. P. György, J. Amer. Chem. Soc., 60, 983 (1938).

5. J.C. Keresztesy and J.R. Stevens, J. Amer. Chem. Soc., 60, 1287 (1938).

6. S. Lepkovsky, Science, 87, 169(1938).

7. Reference 1. pp. 162-172.

8. A.E. Braunstein in The Enzymes, 2nd ed., Vol. II, P.D. Boyer, H. Lardy and K. Myrbäch, eds. Academic Press, New York, N.Y. (1960). p. 113.

9. J.E. Churchich and J.G. Farelly, Biochem. Biophys. Res. Commun., 31, 316 (1968).

10. P. Fasella, Annu. Rev. Biochem., 36, 185 (1967).

11. E. E. Snell and S. J. Di Mari in The Enzymes, 3rd ed., Vol. II, P. D. Boyer, Ed., Academic Press, New York, N.Y. (1970). p. 335.

12. J.N. Lowe and L.L. Ingraham, An Introduction to Biochemical Reaction Mechanisms, Prentice-Hall, Inc., Englewood Cliffs, N.J. (1974). p. 49.

13. H.C. Dunathan, Advan. Enzymol. Relat. Areas Mol. Biol., 35, 79 (1971).

14. Reference 12. pp. 1-23.

15. R. H. Holm in Inorganic Biochemistry, Vol. 2, G.L. Eichhorn, ed., Elsevier Scientific Publishing Company, New York, N.Y. (1973). p. 1137.

16. J.B. Longenecker and E. E. Snell, J. Amer. Chem. Soc., 79, 142 (1957).

17. D.L. Leussing and C.K. Stanfield, J. Amer. Chem. Soc., 88, 5726 (1966).

18. Y. Matsushima and A. E. Martell, J. Amer. Chem. Soc., 89, 1331 (1967).

19. M. E. Farago and T. Matthews, J. Chem. Soc. A, 609 (1969).

20. K. S. Bai and D. L. Leussing, J. Amer. Chem. Soc., 89, 6126 (1967).

21. D. Hopgood and D. L. Leussing, J. Amer. Chem. Soc., 91, 3740 (1969).

22. D. L. Leussing in Metal Ions in Biological Systems, Vol. 5, Helmut Sigel, ed., Marcel Dekker, Inc., New York, N.Y. (1976). p. 72.

23. J.W. Thanassi, Biochemistry, 12, 5109 (1973).

24. K. Tatsumoto and A.E. Martell, J. Amer. Chem. Soc., 99, 6082 (1977).

25. S.W. Tenenbaum, T.H. Withrup and E.H. Abbott, Biochim. Biophys. Acta, 362, 208 (1974).

26. M. Blum and J. W. Thanassi, Bioorg. Chem., 6, 31 (1977).

27. H. N. Christensen, J. Amer. Chem. Soc., 79, 4073 (1957).

28. J.F. Cutfield, D. Hall and T.N. Waters, Chem. Commun., 785 (1967).

29. G.A. Bentley, J.M. Waters and T.N. Waters, Chem. Commun., 988 (1968).

30. E. Willstadter, T. A. Hamor and J. L. Hoard, J. Amer. Chem. Soc., 85, 1205 (1963).

31. S. Capasso, F. Giordano, C. Mattia, L. Mazzarella and A. Ripamonti, J. Chem. Soc., Dalton Trans., 2228 (1974).

32. Reference 15. p. 1152

33. R.L. Gustafson and A.E. Martell, Arch. Biochem. Biophys., 68, 485 (1957).

34. O. A. Gansow and R. H. Holm, Tetrahedron 24, 4477 (1968).

35. V. R. Williams and J. B. Nielands, Arch. Biochem. Biophys., 53, 56 (1954).

36. P. A. Pella and W. C. Purdy, J. Electroanal. Chem., 10, 51 (1965).

37. M. S. El-Ezaby and F. R. El-Eziri, J. Inorg. Nucl. Chem., 38, 1901 (1976).

38. Y. Matsushima and A. E. Martell, J. Amer. Chem. Soc., 89, 1322 (1967).

39. M. S. El-Ezaby, M. Rashad and N. M. Moussa, J. Inorg. Nucl. Chem., 38, 1901 (1976).

40. B. A. Abd-El-Nabey and M. S. El-Ezaby, J. Inorg. Nucl. Chem., 40, 739 (1978).

41. T. A. Figg, "Metal Complexes Involving Vitamin B_6", Honours B.Sc. Thesis, Brock University, St. Catharines, Ontario (1976). p. 18.

42. G. H. Stout and L. H. Jensen, X-ray Structure Determination, The Macmillan Company, New York, N.Y. (1968). p. 90.

43. Ibid. p. 114.

44. Ibid. p. 132.

45. M.H. Buerger, The Precession Method, John Wiley and Sons, Inc., New York, N.Y. (1964). pp. 28, 61.

46. Reference 42. p. 190.

47. Ibid. p. 37.

48. Ibid. p. 31.

49. Ibid. p. 454.

50. International Tables for X-ray Crystallography, Vol. IV. The Kynoch Press, Birmingham, England (1968). pp. 99, 149.

51. W.R. Busing, K.O. Martin and H.A. Levy, ORFLS, Oak Ridge National Laboratory Report ORNL-TM-305, Oak Ridge, Tennessee (1962).

52. A. L. Zalkin, FORDAP, Lawrence Radiation Laboratories, Livermore, California (1962).

53. J.M. Stewart, G.J. Kruger, H.L. Ammon, C. Dickinson and S.R. Hall. The X-RAY SYSTEM of Crystallographic Programs, Computer Science Centre, University of Maryland (1972).

54. International Tables for X-ray Crystallography, Vol. II. The Kynoch Press, Birmingham, England (1959). p. 355.

55. G. M. Sheldrick, SHELX-76, University Chemical Laboratory, Cambridge, England (1976).

56. D. M. Thompson and M. F. Richardson, Acta Crystallogr. Sect. B, 33, 324 (1977).

57. R. B. Wilson, J. R. Wasson, W. E. Hatfield and D. J. Hodgson, Inorg. Chem., 17, 641 (1978).

58. O. Kennard in International Tables for X-ray Crystallography, Vol. III, The Kynoch Press, Birmingham, England (1968). p. 275.

59. C. Singh, Acta Crystallogr. 19, 861 (1965).

60. A.N. Barrett and R.A. Palmer, Acta Crystallogr. Sect. B, 25, 688 (1969).

61. T. Fujiwara, Bull. Chem. Soc. Jap. 46, 863 (1973).

62. F. Hanic, Acta Crystallogr., 21, 332 (1966).

63. F. Giordano and L. Mazzarella, Acta Crystallogr. Sect. B, 27, 128 (1971).

64. J. Gage, I. B. Bersuker, J. Garaj, M. Kabesova, J. Kohout, H. Langfelderova M. Melnick, M. Serator and F. Valach, Coord. Chem. Rev., 19, 253 (1976).

65. S.C. Wallwork and W.E. Addison, J. Chem. Soc. London, 2925 (1965).

66. A. F. Cameron, K. P. Forrest, D. W. Taylor and R. H. Nuttall, J. Chem. Soc. A, 2492 (1971).

67. J. H. Meiners, J.C. Clardy and J. G. Verkade, Inorg. Chem., 14, 632 (1975).

APPENDIX A

OBSERVED AND CALCULATED STRUCTURE FACTORS

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR BIS(PYRIDOXAMINE)COPPER(II) NITRATE.H_2O

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
1	0	0	573	581	-8	2	0	264	269	8	3	0	43	38	1	5	0	89	68	-6	8	0	357	362
2	0	0	444	484	-7	2	0	163	199	11	3	0	55	50	2	5	0	60	-67	-5	8	0	315	326
3	0	0	577	607	-6	2	0	260	274	-14	4	0	186	179	4	5	0	73	-72	-4	8	0	172	184
4	0	0	123	147	-5	2	0	903	921	-13	4	0	327	336	6	5	0	79	-56	-3	8	0	163	172
5	0	0	750	771	-4	2	0	391	-381	-12	4	0	423	431	7	5	0	72	-76	-2	8	0	96	102
6	0	0	427	438	-3	2	0	96	102	-11	4	0	182	174	-13	6	0	111	116	-1	8	0	277	274
8	0	0	214	217	-2	2	0	307	319	-10	4	0	374	373	-12	6	0	104	92	0	8	0	155	160
9	0	0	483	471	-1	2	0	243	243	-9	4	0	355	356	-11	6	0	51	-40	1	8	0	109	106
10	0	0	626	609	0	2	0	1467	1617	-8	4	0	200	223	-9	6	0	43	141	2	8	0	187	194
11	0	0	400	414	1	2	0	824	864	-7	4	0	478	515	-8	6	0	182	183	3	8	0	150	139
12	0	0	257	241	2	2	0	1813	-1895	-6	4	0	390	404	-7	6	0	218	224	4	8	0	291	301
13	0	0	291	289	3	2	0	367	386	-5	4	0	741	729	-6	6	0	421	436	5	8	0	324	330
14	0	0	79	100	4	2	0	231	209	-4	4	0	254	271	-5	6	0	355	364	-3	9	0	76	-43
-14	1	0	64	70	5	2	0	345	342	-2	4	0	552	567	-4	6	0	245	266	-2	9	0	45	-23
-12	1	0	84	-81	6	2	0	168	182	-1	4	0	337	322	-2	6	0	122	117	0	-9	1	57	43
-10	1	0	74	-86	7	2	0	58	81	0	4	0	727	694	-1	6	0	267	259	2	-9	1	118	122
-7	1	0	83	83	9	2	0	353	350	1	4	0	571	570	0	6	0	111	106	3	-9	1	78	82
-4	1	0	135	-130	10	2	0	428	418	3	4	0	151	146	1	6	0	157	174	4	-9	1	47	35
-3	1	0	157	153	11	2	0	150	154	4	4	0	1270	1360	2	6	0	105	121	5	-9	1	76	68
-2	1	0	163	-163	12	2	0	146	147	5	4	0	570	554	4	6	0	569	599	-5	-8	1	266	291
-1	1	0	156	150	13	2	0	89	97	6	4	0	345	369	5	6	0	455	469	-4	-8	1	239	257
0	1	0	116	-142	14	2	0	160	167	7	4	0	315	319	6	6	0	108	-114	-3	-8	1	163	168
1	1	0	96	100	-15	3	0	57	16	8	4	0	105	111	7	6	0	114	109	-2	-8	1	149	147
2	1	0	76	-86	-14	3	0	96	97	9	4	0	274	277	8	6	0	43	29	-1	-8	1	174	165
3	1	0	178	-173	-12	3	0	64	-76	10	4	0	303	289	9	6	0	98	91	0	-8	1	193	187
4	1	0	32	40	-11	3	0	50	-50	11	4	0	86	86	-10	7	0	86	101	1	-8	1	238	242
5	1	0	238	-253	-9	3	0	60	-65	12	4	0	111	94	-8	7	0	74	40	2	-8	1	130	143
6	1	0	87	84	-8	3	0	70	84	-12	5	0	109	-113	-4	7	0	48	56	3	-8	1	118	120
8	1	0	46	58	-6	3	0	102	103	-11	5	0	51	-22	-3	7	0	66	-57	4	-8	1	230	225
11	1	0	48	55	-5	3	0	162	-172	-8	5	0	91	-88	-2	7	0	64	50	5	-8	1	261	259
-15	2	0	55	30	-4	3	0	146	145	-7	5	0	87	87	2	7	0	42	5	6	-8	1	246	243
-13	2	0	280	286	-3	3	0	150	-160	-6	5	0	111	-113	5	7	0	71	80	7	-8	1	275	282
-12	2	0	303	300	-2	3	0	197	195	-5	5	0	52	76	7	7	0	81	-38	8	-8	1	291	291
-11	2	0	195	198	-1	3	0	73	-77	-4	5	0	55	-50	-9	8	0	233	233	9	-8	1	107	113
-10	2	0	596	592	0	3	0	100	123	-3	5	0	58	47	-8	8	0	338	353	-7	-7	1	45	52
-9	2	0	198	196	1	3	0	133	131	-1	5	0	63	63	-7	8	0	271	280	-6	-7	1	99	-97

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-5	-7	1	100	-111	-8	-5	1	66	55	4	-4	1	498	475	-13	-2	1	123	124	-3	-1	1	1157	1171
-4	-7	1	109	-107	-7	-5	1	131	139	5	-4	1	729	724	-12	-2	1	171	163	-2	-1	1	129	138
-3	-7	1	116	118	-6	-5	1	51	35	6	-4	1	459	461	-11	-2	1	134	144	-1	-1	1	216	-212
-2	-7	1	51	-52	-4	-5	1	135	124	7	-4	1	262	274	-10	-2	1	354	342	0	-1	1	244	234
-1	-7	1	62	28	-3	-5	1	381	377	8	-4	1	386	384	-9	-2	1	401	412	1	-1	1	494	489
1	-7	1	72	-66	-2	-5	1	155	164	9	-4	1	285	293	-8	-2	1	100	111	2	-1	1	689	682
2	-7	1	61	43	-1	-5	1	241	-224	10	-4	1	178	185	-7	-2	1	217	222	3	-1	1	478	-488
4	-7	1	122	-128	0	-5	1	150	152	11	-4	1	271	282	-6	-2	1	289	296	4	-1	1	817	825
6	-7	1	109	-114	1	-5	1	324	-324	12	-4	1	286	295	-5	-2	1	201	214	5	-1	1	140	-140
7	-7	1	111	-117	4	-5	1	65	52	13	-4	1	168	160	-4	-2	1	751	795	6	-1	1	45	44
9	-7	1	109	-105	5	-5	1	57	-49	14	-4	1	89	82	-3	-2	1	46	46	7	-1	1	318	298
11	-7	1	50	-29	6	-5	1	239	235	-11	-3	1	162	-164	-2	-2	1	359	366	8	-1	1	189	-192
-9	-6	1	70	74	7	-5	1	179	183	-9	-3	1	105	-117	-1	-2	1	487	478	10	-1	1	76	67
-8	-6	1	78	80	8	-5	1	66	72	-7	-3	1	185	-202	0	-2	1	1230	1228	11	-1	1	65	-43
-7	-6	1	72	74	9	-5	1	179	183	-6	-3	1	50	38	1	-2	1	338	341	15	-1	1	123	118
-6	-6	1	93	96	10	-5	1	45	-26	-5	-3	1	203	-206	2	-2	1	420	410	-15	0	1	57	47
-5	-6	1	370	378	11	-5	1	64	72	-4	-3	1	112	-109	3	-2	1	295	292	-14	0	1	109	100
-4	-6	1	467	482	12	-5	1	47	-50	-3	-3	1	381	365	4	-2	1	355	350	-13	0	1	205	198
-3	-6	1	99	112	13	-5	1	47	-44	-2	-3	1	398	-399	5	-2	1	325	313	-12	0	1	316	315
-2	-6	1	201	190	14	-5	1	188	191	-1	-3	1	732	-680	6	-2	1	228	217	-11	0	1	360	362
-1	-6	1	164	162	-12	-4	1	93	103	0	-3	1	658	-633	7	-2	1	75	-63	-10	0	1	496	517
0	-6	1	213	204	-11	-4	1	74	85	1	-3	1	55	-68	8	-2	1	319	332	-9	0	1	678	674
1	-6	1	159	164	-10	-4	1	238	238	2	-3	1	448	-447	9	-2	1	314	329	-8	0	1	218	238
2	-6	1	73	77	-9	-4	1	225	227	3	-3	1	134	132	10	-2	1	294	311	-7	0	1	251	263
3	-6	1	75	64	-8	-4	1	97	111	4	-3	1	222	207	11	-2	1	285	282	-6	0	1	242	259
4	-6	1	271	255	-7	-4	1	305	300	5	-3	1	109	113	12	-2	1	331	333	-5	0	1	395	421
5	-6	1	405	389	-6	-4	1	234	232	6	-3	1	204	196	13	-2	1	219	213	-4	0	1	269	274
6	-6	1	323	336	-5	-4	1	533	547	7	-3	1	405	384	14	-2	1	73	67	-3	0	1	600	617
7	-6	1	262	264	-4	-4	1	679	686	8	-3	1	245	-247	15	-2	1	166	170	-2	0	1	106	112
8	-6	1	321	315	-3	-4	1	278	296	9	-3	1	47	-26	-11	-1	1	71	-59	-1	0	1	882	846
9	-6	1	148	144	-2	-4	1	135	141	10	-3	1	159	-151	-10	-1	1	106	-105	0	0	1	1089	1115
10	-6	1	79	67	-1	-4	1	596	576	11	-3	1	276	-272	-9	-1	1	100	85	1	0	1	950	1006
11	-6	1	204	208	0	-4	1	411	417	13	-3	1	231	-230	-7	-1	1	40	16	2	0	1	63	64
12	-6	1	192	202	1	-4	1	566	584	14	-3	1	96	100	-6	-1	1	140	154	3	0	1	681	710
13	-6	1	110	110	2	-4	1	211	213	15	-3	1	48	44	-5	-1	1	569	569	4	0	1	257	273
-10	-5	1	51	31	3	-4	1	493	489	-14	-2	1	155	141	-4	-1	1	92	81	5	0	1	408	443

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
6	0	1	282	308	-13	2	1	225	218	-6	3	1	324	-310	6	4	1	185	178	0	6	1	256	252
7	0	1	265	269	-12	2	1	352	347	-5	3	1	152	152	7	4	1	266	276	1	6	1	154	140
8	0	1	413	420	-11	2	1	302	311	-4	3	1	332	-329	8	4	1	156	156	2	6	1	247	250
9	0	1	541	537	-10	2	1	353	364	-3	3	1	136	141	9	4	1	161	164	3	6	1	148	130
10	0	1	388	402	-9	2	1	372	386	-1	3	1	619	623	10	4	1	196	203	4	6	1	261	269
11	0	1	282	285	-8	2	1	195	207	0	3	1	192	186	11	4	1	79	76	5	6	1	403	414
12	0	1	279	276	-7	2	1	51	-31	1	3	1	890	875	12	4	1	148	150	6	6	1	139	151
13	0	1	225	224	-6	2	1	195	200	2	3	1	362	360	-12	5	1	75	75	7	6	1	165	170
14	0	1	92	80	-5	2	1	354	344	3	3	1	319	-328	-10	5	1	126	-130	8	6	1	119	128
15	0	1	126	119	-4	2	1	307	319	4	3	1	33	38	-9	5	1	78	-73	9	6	1	119	117
-14	1	1	157	-159	-3	2	1	230	223	6	3	1	39	-32	-8	5	1	90	-88	-11	7	1	77	63
-12	1	1	58	-37	-2	2	1	508	521	8	3	1	190	184	-7	5	1	197	-206	-9	7	1	66	67
-11	1	1	50	-12	-1	2	1	257	265	9	3	1	71	79	-6	5	1	103	-107	-8	7	1	101	113
-8	1	1	231	225	0	2	1	1125	1144	10	3	1	133	145	-5	5	1	137	-144	-7	7	1	70	68
-7	1	1	473	-475	1	2	1	700	687	11	3	1	129	144	-4	5	1	73	63	-6	7	1	101	115
-6	1	1	196	186	2	2	1	505	503	12	3	1	44	-13	-3	5	1	199	-195	-5	7	1	55	51
-5	1	1	170	-188	3	2	1	294	295	-14	4	1	116	114	-2	5	1	53	57	-4	7	1	84	92
-4	1	1	114	-114	4	2	1	556	590	-13	4	1	183	179	-1	5	1	135	136	-3	7	1	42	-20
-3	1	1	262	-262	5	2	1	430	453	-12	4	1	285	275	3	5	1	387	-386	-2	7	1	55	-53
-2	1	1	92	-83	6	2	1	295	298	-11	4	1	187	189	4	5	1	154	-148	-1	7	1	96	95
-1	1	1	746	-759	7	2	1	341	338	-10	4	1	205	205	6	5	1	67	-72	1	7	1	42	25
0	1	1	226	-222	8	2	1	246	248	-9	4	1	215	229	7	5	1	140	-138	2	7	1	46	39
1	1	1	267	263	9	2	1	313	320	-8	4	1	319	332	10	5	1	50	-58	3	7	1	47	43
2	1	1	168	-164	10	2	1	247	261	-7	4	1	268	283	11	5	1	66	46	4	7	1	45	34
3	1	1	868	-889	11	2	1	100	105	-6	4	1	415	437	-12	6	1	184	187	5	7	1	146	158
4	1	1	372	-379	12	2	1	184	189	-5	4	1	816	817	-11	6	1	179	184	6	7	1	63	71
5	1	1	223	-214	13	2	1	161	149	-4	4	1	471	471	-10	6	1	143	142	7	7	1	62	-60
6	1	1	575	-586	14	2	1	117	123	-3	4	1	515	515	-9	6	1	178	176	-9	8	1	55	50
7	1	1	95	96	-14	3	1	72	-77	-2	4	1	330	348	-8	6	1	360	358	-8	8	1	233	226
8	1	1	109	-117	-13	3	1	93	94	-1	4	1	400	422	-7	6	1	313	323	-7	8	1	201	209
10	1	1	133	134	-12	3	1	167	188	0	4	1	488	507	-6	6	1	313	331	-6	8	1	144	138
11	1	1	70	68	-11	3	1	170	164	1	4	1	374	382	-5	6	1	460	476	-5	8	1	224	227
13	1	1	46	-44	-10	3	1	98	107	2	4	1	280	269	-4	6	1	229	230	-4	8	1	139	136
14	1	1	48	-19	-9	3	1	123	125	3	4	1	116	130	-3	6	1	115	116	-3	8	1	123	123
-15	2	1	81	78	-8	3	1	65	42	4	4	1	350	349	-2	6	1	68	91	-2	8	1	113	103
-14	2	1	89	88	-7	3	1	157	-155	5	4	1	443	453	-1	6	1	122	133	-1	8	1	195	200

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR BIS(PYRIDOXAMINE)COPPER(II) NITRATE.H_2O

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
0	8	1	244	241	6	-7	2	116	-117	5	-5	2	351	346	-10	-3	2	139	-149	2	-2	2	678	682
1	8	1	131	138	7	-7	2	98	-94	6	-5	2	199	192	-9	-3	2	163	-158	3	-2	2	408	405
2	8	1	172	186	8	-7	2	100	103	7	-5	2	71	66	-8	-3	2	124	-112	4	-2	2	549	564
3	8	1	97	127	9	-7	2	66	78	8	-5	2	162	158	-6	-3	2	150	136	5	-2	2	348	367
4	8	1	113	140	-9	-6	2	172	172	9	-5	2	81	85	-5	-3	2	412	398	6	-2	2	504	523
5	8	1	217	230	-8	-6	2	139	134	10	-5	2	115	-116	-4	-3	2	80	70	7	-2	2	333	333
-4	9	1	50	-43	-7	-6	2	171	170	11	-5	2	189	-204	-3	-3	2	237	223	8	-2	2	494	481
-3	9	1	75	-67	-6	-6	2	222	216	12	-5	2	81	-94	-1	-3	2	336	-328	9	-2	2	298	294
-2	9	1	124	-125	-5	-6	2	292	302	-12	-4	2	119	110	0	-3	2	68	-53	10	-2	2	219	217
-1	9	1	66	-54	-4	-6	2	241	247	-11	-4	2	161	159	1	-3	2	703	-666	11	-2	2	135	129
1	-9	2	94	96	-3	-6	2	246	247	-10	-4	2	116	112	2	-3	2	419	-383	12	-2	2	270	278
2	-9	2	130	128	-2	-6	2	238	239	-9	-4	2	191	198	3	-3	2	143	-137	13	-2	2	341	349
3	-9	2	56	56	-1	-6	2	362	350	-8	-4	2	212	204	4	-3	2	135	-119	14	-2	2	132	135
4	-9	2	53	62	0	-6	2	180	179	-7	-4	2	57	51	5	-3	2	147	145	15	-2	2	215	202
5	-9	2	49	49	1	-6	2	257	240	-6	-4	2	386	389	6	-3	2	99	88	-14	-1	2	52	52
-5	-8	2	164	167	2	-6	2	288	276	-5	-4	2	59	61	8	-3	2	129	-132	-13	-1	2	48	10
-4	-8	2	125	124	3	-6	2	174	176	-4	-4	2	372	367	9	-3	2	41	24	-10	-1	2	84	-86
-3	-8	2	131	133	4	-6	2	427	432	-3	-4	2	111	105	10	-3	2	177	-182	-9	-1	2	156	-134
-2	-8	2	131	143	5	-6	2	186	187	-2	-4	2	249	276	11	-3	2	263	-258	-8	-1	2	157	167
-1	-8	2	205	217	6	-6	2	229	235	-1	-4	2	387	402	14	-3	2	72	59	-7	-1	2	83	73
0	-8	2	155	143	7	-6	2	234	231	0	-4	2	195	194	-14	-2	2	141	136	-6	-1	2	325	291
1	-8	2	192	190	8	-6	2	359	371	1	-4	2	376	370	-13	-2	2	174	166	-5	-1	2	363	338
2	-8	2	126	124	9	-6	2	422	436	2	-4	2	459	452	-12	-2	2	184	195	-4	-1	2	60	-51
3	-8	2	172	162	10	-6	2	102	105	3	-4	2	352	357	-11	-2	2	247	246	-3	-1	2	91	-86
4	-8	2	219	222	11	-6	2	293	290	4	-4	2	456	458	-10	-2	2	177	183	-1	-1	2	189	-179
5	-8	2	143	141	12	-6	2	240	239	5	-4	2	347	344	-9	-2	2	321	312	0	-1	2	81	-79
7	-8	2	71	52	-8	-5	2	44	-25	6	-4	2	217	228	-8	-2	2	377	392	1	-1	2	524	-529
8	-8	2	208	211	-6	-5	2	44	54	7	-4	2	333	348	-7	-2	2	235	241	2	-1	2	297	-284
9	-8	2	122	119	-5	-5	2	104	111	8	-4	2	295	293	-6	-2	2	464	474	3	-1	2	118	129
-5	-7	2	78	-70	-4	-5	2	97	85	9	-4	2	369	364	-5	-2	2	607	608	4	-1	2	393	354
-4	-7	2	43	-60	-3	-5	2	205	196	10	-4	2	66	68	-4	-2	2	318	292	5	-1	2	264	246
1	-7	2	129	-120	-2	-5	2	51	36	11	-4	2	74	58	-3	-2	2	896	919	6	-1	2	290	261
2	-7	2	43	62	-1	-5	2	64	55	12	-4	2	285	288	-2	-2	2	259	275	7	-1	2	132	128
3	-7	2	61	-56	0	-5	2	112	102	13	-4	2	129	124	-1	-2	2	1021	1019	9	-1	2	166	167
4	-7	2	78	-77	1	-5	2	146	-131	14	-4	2	163	154	0	-2	2	421	392	10	-1	2	80	84
5	-7	2	47	50	3	-5	2	175	182	-11	-3	2	102	-113	1	-2	2	721	714	11	-1	2	145	-135

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
12	-1	2	61	36	-9	1	2	180	-189	3	2	2	681	696	-9	4	2	289	291	5	5	2	90	-83
13	-1	2	77	79	-8	1	2	41	39	4	2	2	418	406	-8	4	2	166	174	7	5	2	60	72
15	-1	2	67	-35	-7	1	2	132	-123	5	2	2	450	451	-7	4	2	431	435	9	5	2	53	57
-14	0	2	50	36	-6	1	2	391	-376	6	2	2	514	552	-6	4	2	80	90	-12	6	2	234	236
-13	0	2	214	216	-5	1	2	196	-165	7	2	2	248	270	-5	4	2	274	275	-11	6	2	290	294
-12	0	2	194	189	-4	1	2	609	-577	8	2	2	401	419	-4	4	2	454	466	-10	6	2	94	89
-11	0	2	310	310	-2	1	2	192	180	9	2	2	243	238	-3	4	2	231	246	-9	6	2	255	251
-10	0	2	194	188	-1	1	2	582	569	10	2	2	231	209	-2	4	2	353	361	-8	6	2	333	330
-9	0	2	328	322	0	1	2	277	273	11	2	2	177	187	-1	4	2	401	394	-7	6	2	266	265
-8	0	2	421	431	1	1	2	162	148	12	2	2	181	172	0	4	2	136	122	-6	6	2	236	225
-7	0	2	295	303	2	1	2	170	160	13	2	2	197	204	1	4	2	384	371	-5	6	2	161	165
-6	0	2	304	316	3	1	2	98	96	-14	3	2	137	-146	2	4	2	257	264	-4	6	2	438	433
-5	0	2	479	479	4	1	2	128	125	-13	3	2	50	32	3	4	2	177	183	-3	6	2	305	304
-4	0	2	380	375	5	1	2	328	-309	-11	3	2	119	101	4	4	2	236	240	-2	6	2	320	322
-3	0	2	39	49	6	1	2	318	-304	-10	3	2	276	267	5	4	2	161	163	-1	6	2	321	310
-2	0	2	658	648	7	1	2	69	-64	-8	3	2	199	207	6	4	2	233	243	0	6	2	338	335
-1	0	2	143	-128	8	1	2	168	-166	-6	3	2	155	-139	7	4	2	163	153	1	6	2	282	274
0	0	2	523	528	9	1	2	141	136	-5	3	2	131	-132	8	4	2	224	230	2	6	2	354	350
1	0	2	67	71	11	1	2	57	-30	-4	3	2	65	47	9	4	2	229	218	3	6	2	209	206
2	0	2	288	281	-14	2	2	109	97	-3	3	2	170	158	10	4	2	161	148	4	6	2	143	148
3	0	2	338	336	-13	2	2	202	194	-2	3	2	307	274	11	4	2	142	151	5	6	2	206	217
4	0	2	252	252	-12	2	2	405	410	-1	3	2	625	584	12	4	2	93	105	6	6	2	144	137
5	0	2	525	524	-11	2	2	224	221	0	3	2	187	170	-13	5	2	63	59	7	6	2	178	174
6	0	2	422	435	-10	2	2	332	329	1	3	2	98	85	-12	5	2	104	112	8	6	2	182	188
7	0	2	376	378	-9	2	2	248	253	2	3	2	121	120	-11	5	2	137	144	9	6	2	188	200
8	0	2	333	352	-8	2	2	456	451	3	3	2	281	-261	-10	5	2	153	156	-10	7	2	60	-64
9	0	2	270	263	-7	2	2	428	446	4	3	2	96	-91	-8	5	2	116	-107	-9	7	2	72	-84
10	0	2	85	83	-6	2	2	253	271	5	3	2	403	-390	-7	5	2	68	-79	-8	7	2	86	-102
11	0	2	169	166	-5	2	2	502	516	6	3	2	239	-233	-6	5	2	155	-144	-6	7	2	117	119
12	0	2	100	107	-4	2	2	618	636	9	3	2	152	146	-5	5	2	291	-281	-3	7	2	84	96
13	0	2	301	300	-3	2	2	291	290	10	3	2	60	76	-4	5	2	84	-71	-2	7	2	102	-98
14	0	2	127	134	-2	2	2	796	806	11	3	2	61	49	-3	5	2	53	-68	-1	7	2	98	92
-14	1	2	74	-69	-1	2	2	617	622	-14	4	2	142	136	-2	5	2	163	-172	3	7	2	64	44
-12	1	2	96	-94	0	2	2	334	324	-12	4	2	315	323	-1	5	2	147	136	7	7	2	50	8
-11	1	2	67	59	1	2	2	854	854	-11	4	2	185	185	1	5	2	136	-123	-8	8	2	253	253
-10	1	2	55	-49	2	2	2	238	256	-10	4	2	48	53	3	5	2	135	-127	-7	8	2	141	143

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-6	8	2	69	68	-5	-6	3	134	132	-10	-4	3	191	197	9	-3	3	67	40	-8	-1	3	140	-142
-5	8	2	111	123	-4	-6	3	145	144	-9	-4	3	155	154	10	-3	3	160	155	-6	-1	3	141	138
-4	8	2	180	180	-3	-6	3	198	200	-8	-4	3	347	339	11	-3	3	247	-252	-5	-1	3	205	194
-2	8	2	100	98	-2	-6	3	190	193	-7	-4	3	264	257	12	-3	3	53	12	-4	-1	3	108	100
-1	8	2	150	133	-1	-6	3	401	414	-6	-4	3	107	115	14	-3	3	54	50	-3	-1	3	220	202
0	8	2	161	160	0	-6	3	504	498	-5	-4	3	214	218	-13	-2	3	298	299	-2	-1	3	466	-457
1	8	2	163	160	1	-6	3	329	319	-4	-4	3	301	303	-12	-2	3	175	170	-1	-1	3	43	55
2	8	2	141	142	2	-6	3	400	406	-3	-4	3	363	364	-11	-2	3	144	147	0	-1	3	127	-116
3	8	2	123	119	3	-6	3	451	433	-2	-4	3	216	221	-10	-2	3	244	235	1	-1	3	444	-442
4	8	2	46	28	4	-6	3	340	331	-1	-4	3	448	420	-9	-2	3	264	264	2	-1	3	517	485
-4	-8	3	61	64	5	-6	3	293	277	0	-4	3	440	428	-8	-2	3	309	306	3	-1	3	146	-160
-3	-8	3	72	74	6	-6	3	160	160	1	-4	3	159	165	-7	-2	3	410	420	4	-1	3	165	150
-2	-8	3	62	47	8	-6	3	105	98	2	-4	3	74	88	-6	-2	3	302	301	5	-1	3	135	137
-1	-8	3	194	209	9	-6	3	356	365	3	-4	3	282	271	-5	-2	3	177	189	6	-1	3	357	-337
1	-8	3	87	90	11	-6	3	137	139	4	-4	3	357	350	-4	-2	3	647	629	7	-1	3	150	146
2	-8	3	197	197	12	-6	3	213	201	6	-4	3	200	203	-3	-2	3	436	414	8	-1	3	68	-64
3	-8	3	143	143	-8	-5	3	70	-69	8	-4	3	113	112	-2	-2	3	147	155	9	-1	3	88	-78
4	-8	3	211	201	-7	-5	3	43	43	9	-4	3	550	547	-1	-2	3	395	377	10	-1	3	48	49
5	-8	3	236	234	-6	-5	3	62	-78	10	-4	3	328	334	0	-2	3	63	67	11	-1	3	78	-89
6	-8	3	90	95	-4	-5	3	145	147	11	-4	3	108	104	1	-2	3	325	320	12	-1	3	129	-125
8	-8	3	131	126	-3	-5	3	148	-141	12	-4	3	173	161	3	-2	3	714	727	13	-1	3	114	112
-5	-7	3	43	39	-2	-5	3	228	229	13	-4	3	227	229	4	-2	3	1122	1107	-14	0	3	137	136
-4	-7	3	59	-64	-1	-5	3	62	-57	14	-4	3	207	204	5	-2	3	469	472	-13	0	3	305	301
-1	-7	3	69	63	1	-5	3	69	-62	-11	-3	3	59	-78	6	-2	3	564	556	-12	0	3	169	174
0	-7	3	57	70	2	-5	3	241	-234	-10	-3	3	44	-40	7	-2	3	548	548	-9	0	3	247	254
2	-7	3	68	-71	3	-5	3	134	128	-9	-3	3	51	-50	8	-2	3	308	324	-8	0	3	158	155
3	-7	3	84	71	4	-5	3	105	101	-8	-3	3	104	-113	9	-2	3	560	564	-7	0	3	315	305
6	-7	3	129	121	6	-5	3	87	88	-6	-3	3	120	124	10	-2	3	311	314	-6	0	3	587	570
7	-7	3	219	-220	8	-5	3	135	-126	-5	-3	3	74	85	11	-2	3	63	-58	-5	0	3	47	56
8	-7	3	82	85	9	-5	3	243	249	-4	-3	3	423	434	13	-2	3	280	268	-4	0	3	988	981
9	-7	3	93	92	10	-5	3	101	-90	-1	-3	3	191	197	14	-2	3	254	247	-3	0	3	777	786
10	-7	3	57	59	11	-5	3	69	-60	0	-3	3	535	-504	-14	-1	3	100	86	-2	0	3	230	250
-9	-6	3	155	138	12	-5	3	110	-103	2	-3	3	200	-194	-13	-1	3	150	-151	-1	0	3	447	442
-8	-6	3	296	292	13	-5	3	47	-24	4	-3	3	417	385	-12	-1	3	77	-52	0	0	3	72	84
-7	-6	3	145	143	-12	-4	3	91	78	5	-3	3	39	-35	-11	-1	3	72	65	1	0	3	270	270
-6	-6	3	123	114	-11	-4	3	142	141	7	-3	3	65	73	-10	-1	3	113	-117	2	0	3	403	417

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
3	0	3	443	453	14	1	3	60	60	-4	3	3	347	-334	-12	5	3	48	36	-7	7	3	69	69
4	0	3	1232	1209	-14	2	3	182	177	-3	3	3	213	-195	-11	5	3	90	102	-6	7	3	180	181
5	0	3	268	261	-13	2	3	224	225	-2	3	3	79	85	-10	5	3	124	118	-5	7	3	116	-116
6	0	3	303	319	-12	2	3	231	233	0	3	3	314	313	-9	5	3	113	-124	-4	7	3	43	14
7	0	3	339	347	-11	2	3	79	75	1	3	3	84	89	-8	5	3	207	-202	-3	7	3	45	-40
8	0	3	289	280	-10	2	3	43	43	2	3	3	127	-130	-7	5	3	179	171	0	7	3	88	-89
9	0	3	226	225	-9	2	3	528	530	3	3	3	133	121	-2	5	3	125	133	1	7	3	103	-100
10	0	3	119	122	-8	2	3	444	439	4	3	3	195	-207	-1	5	3	186	185	-7	8	3	126	105
11	0	3	70	-67	-7	2	3	378	375	5	3	3	58	-50	0	5	3	67	56	-5	8	3	201	196
12	0	3	81	-89	-6	2	3	765	757	6	3	3	98	90	2	5	3	55	-61	-4	8	3	219	222
13	0	3	322	317	-5	2	3	368	380	7	3	3	105	-98	3	5	3	56	-72	-3	8	3	152	147
14	0	3	331	326	-4	2	3	688	690	8	3	3	86	86	5	5	3	80	-86	-2	8	3	196	185
-13	1	3	62	-67	-3	2	3	1084	1077	10	3	3	61	-47	6	5	3	60	64	-1	8	3	105	103
-12	1	3	59	-82	-2	2	3	46	51	-13	4	3	218	206	8	5	3	82	-77	0	8	3	157	152
-11	1	3	244	242	-1	2	3	344	359	-12	4	3	243	241	9	5	3	53	64	1	8	3	235	224
-10	1	3	138	139	0	2	3	35	52	-11	4	3	231	228	10	5	3	72	-60	2	8	3	129	124
-9	1	3	119	-120	1	2	3	456	435	-10	4	3	102	96	-11	6	3	192	196	3	8	3	66	46
-8	1	3	127	121	2	2	3	134	128	-9	4	3	458	462	-10	6	3	144	142	-2	-8	4	58	55
-7	1	3	125	-132	3	2	3	393	379	-8	4	3	393	384	-9	6	3	251	250	-1	-8	4	229	232
-6	1	3	92	83	4	2	3	536	533	-6	4	3	189	198	-8	6	3	293	297	0	-8	4	207	203
-5	1	3	137	126	5	2	3	287	291	-5	4	3	52	71	-5	6	3	217	207	1	-8	4	192	187
-4	1	3	260	-245	6	2	3	114	118	-4	4	3	183	181	-4	6	3	274	271	2	-8	4	169	167
-2	1	3	176	-156	7	2	3	325	327	-3	4	3	346	334	-3	6	3	367	366	3	-8	4	194	187
-1	1	3	169	-164	8	2	3	425	418	-2	4	3	292	293	-2	6	3	405	409	4	-8	4	190	184
0	1	3	615	584	9	2	3	307	292	0	4	3	454	450	-1	6	3	301	304	5	-8	4	224	214
1	1	3	237	-243	10	2	3	159	163	1	4	3	461	438	0	6	3	331	332	6	-8	4	47	36
2	1	3	259	250	11	2	3	143	129	2	4	3	353	340	1	6	3	499	488	-3	-7	4	61	58
3	1	3	149	152	12	2	3	51	31	3	4	3	209	224	2	6	3	179	170	-2	-7	4	41	-30
4	1	3	439	-425	13	2	3	284	272	4	4	3	350	339	3	6	3	147	151	0	-7	4	116	111
5	1	3	165	159	-14	3	3	87	-82	5	4	3	127	124	4	6	3	86	68	1	-7	4	132	134
6	1	3	248	-245	-13	3	3	54	-36	6	4	3	117	108	5	6	3	84	82	3	-7	4	67	63
8	1	3	164	153	-11	3	3	154	158	7	4	3	163	162	6	6	3	52	67	6	-7	4	92	92
9	1	3	64	-76	-10	3	3	282	277	8	4	3	406	398	7	6	3	130	118	7	-7	4	53	44
10	1	3	56	74	-9	3	3	262	-260	9	4	3	253	256	8	6	3	277	271	8	-7	4	160	-150
11	1	3	48	59	-8	3	3	45	-47	10	4	3	115	113	-9	7	3	91	-85	-8	-6	4	271	271
12	1	3	55	-32	-6	3	3	215	-215	11	4	3	143	144	-8	7	3	55	-48	-7	-6	4	240	244

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-6	-6	4	56	71	-4	-4	4	176	163	11	-3	4	194	195	-6	-1	4	110	102	8	0	4	250	259
-5	-6	4	95	83	-3	-4	4	276	260	12	-3	4	116	-119	-5	-1	4	96	-98	9	0	4	400	388
-3	-6	4	105	96	-2	-4	4	257	261	-13	-2	4	352	345	-4	-1	4	123	-105	10	0	4	108	104
-2	-6	4	148	135	-1	-4	4	453	468	-12	-2	4	138	142	-3	-1	4	100	87	12	0	4	92	104
-1	-6	4	302	292	0	-4	4	475	481	-11	-2	4	45	-40	-2	-1	4	431	404	13	0	4	272	267
0	-6	4	486	486	1	-4	4	342	339	-10	-2	4	135	142	-1	-1	4	34	-32	-13	1	4	92	-99
1	-6	4	195	190	2	-4	4	98	101	-9	-2	4	165	163	0	-1	4	161	150	-12	1	4	120	115
2	-6	4	345	342	3	-4	4	549	525	-8	-2	4	395	390	1	-1	4	462	444	-11	1	4	49	20
3	-6	4	252	245	4	-4	4	303	306	-7	-2	4	400	397	2	-1	4	68	-63	-10	1	4	119	-121
4	-6	4	282	279	5	-4	4	392	387	-6	-2	4	236	228	3	-1	4	221	-189	-9	1	4	46	47
5	-6	4	220	202	6	-4	4	175	173	-5	-2	4	255	262	4	-1	4	47	50	-8	1	4	173	173
6	-6	4	81	74	7	-4	4	157	166	-4	-2	4	503	490	5	-1	4	121	112	-7	1	4	74	80
9	-6	4	298	301	8	-4	4	248	244	-3	-2	4	746	736	7	-1	4	252	-246	-6	1	4	168	164
10	-6	4	241	237	9	-4	4	456	447	-2	-2	4	479	482	9	-1	4	266	-266	-5	1	4	56	-60
11	-6	4	255	253	10	-4	4	194	187	-1	-2	4	409	416	10	-1	4	105	106	-3	1	4	88	-104
-7	-5	4	88	93	11	-4	4	104	113	0	-2	4	416	387	11	-1	4	224	229	-2	1	4	426	384
-6	-5	4	73	84	13	-4	4	113	115	1	-2	4	44	52	12	-1	4	124	-130	-1	1	4	338	-320
-5	-5	4	64	-57	-12	-3	4	108	115	2	-2	4	213	227	13	-1	4	73	-53	0	1	4	398	-386
-4	-5	4	66	70	-9	-3	4	70	51	3	-2	4	276	259	-13	0	4	423	417	1	1	4	89	92
-1	-5	4	90	-97	-8	-3	4	125	-119	4	-2	4	884	854	-12	0	4	115	112	3	1	4	110	-99
0	-5	4	58	61	-7	-3	4	91	86	5	-2	4	228	212	-11	0	4	92	-97	4	1	4	90	-83
1	-5	4	178	170	-6	-3	4	85	78	6	-2	4	402	419	-10	0	4	47	51	5	1	4	319	305
2	-5	4	149	-142	-5	-3	4	203	-200	7	-2	4	187	195	-9	0	4	347	335	6	1	4	64	77
3	-5	4	162	-152	-4	-3	4	93	-93	8	-2	4	278	291	-8	0	4	341	352	7	1	4	185	-181
5	-5	4	175	-172	-3	-3	4	72	-58	9	-2	4	358	357	-7	0	4	435	438	8	1	4	52	44
6	-5	4	135	133	-1	-3	4	157	-156	10	-2	4	151	143	-6	0	4	299	329	9	1	4	71	-70
8	-5	4	43	-60	1	-3	4	452	428	11	-2	4	63	-63	-5	0	4	359	368	11	1	4	141	158
9	-5	4	93	-102	2	-3	4	169	-161	12	-2	4	145	128	-4	0	4	655	636	12	1	4	124	-119
10	-5	4	196	205	3	-3	4	44	-16	13	-2	4	168	180	-3	0	4	879	823	13	1	4	141	-140
11	-5	4	113	103	4	-3	4	43	41	14	-2	4	245	238	-2	0	4	97	106	-13	2	4	281	281
12	-5	4	56	53	5	-3	4	196	191	-13	-1	4	65	-64	0	0	4	274	-246	-12	2	4	140	138
-10	-4	4	148	152	6	-3	4	70	69	-12	-1	4	117	117	3	0	4	466	450	-11	2	4	112	-116
-9	-4	4	148	145	7	-3	4	132	116	-10	-1	4	186	-183	4	0	4	678	674	-10	2	4	117	106
-8	-4	4	362	371	8	-3	4	60	-74	-9	-1	4	86	81	5	0	4	544	539	-9	2	4	383	376
-7	-4	4	273	266	9	-3	4	173	-162	-8	-1	4	105	-113	6	0	4	198	215	-8	2	4	384	390
-6	-4	4	111	107	10	-3	4	158	153	-7	-1	4	76	75	7	0	4	473	489	-7	2	4	96	105

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-6	2	4	345	360	10	3	4	80	-70	2	5	4	99	104	0	-8	5	138	144	2	-5	5	71	69
-5	2	4	157	156	11	3	4	45	8	3	5	4	51	-55	1	-8	5	134	130	3	-5	5	105	97
-4	2	4	648	629	-13	4	4	138	130	4	5	4	71	-79	2	-8	5	145	140	8	-5	5	215	-223
-3	2	4	557	530	-12	4	4	149	156	5	5	4	52	55	3	-8	5	143	147	9	-5	5	89	88
-2	2	4	314	311	-11	4	4	81	79	7	5	4	56	-46	4	-8	5	230	232	11	-5	5	81	78
-1	2	4	53	49	-10	4	4	150	152	-10	6	4	202	200	5	-8	5	110	125	-10	-4	5	163	166
0	2	4	329	317	-9	4	4	491	475	-9	6	4	404	399	-3	-7	5	92	90	-9	-4	5	163	168
1	2	4	496	471	-8	4	4	307	310	-8	6	4	239	251	-1	-7	5	75	-63	-8	-4	5	197	192
2	2	4	519	537	-7	4	4	127	119	-6	6	4	58	64	1	-7	5	42	34	-7	-4	5	190	179
3	2	4	505	513	-6	4	4	132	134	-5	6	4	104	97	6	-7	5	205	212	-6	-4	5	83	91
4	2	4	645	633	-5	4	4	288	289	-4	6	4	309	306	-7	-6	5	208	201	-4	-4	5	90	119
5	2	4	317	318	-4	4	4	340	343	-3	6	4	181	181	-6	-6	5	140	139	-3	-4	5	110	106
6	2	4	239	240	-3	4	4	511	510	-2	6	4	273	268	-5	-6	5	148	143	-2	-4	5	333	325
7	2	4	246	245	-2	4	4	223	228	-1	6	4	185	182	-4	-6	5	97	94	-1	-4	5	190	173
8	2	4	344	335	-1	4	4	350	355	0	6	4	268	261	-3	-6	5	124	125	0	-4	5	308	302
9	2	4	214	217	0	4	4	239	242	1	6	4	308	308	-2	-6	5	240	242	1	-4	5	158	176
10	2	4	149	154	1	4	4	564	560	2	6	4	216	214	-1	-6	5	238	232	2	-4	5	390	386
11	2	4	57	45	2	4	4	263	265	3	6	4	84	78	0	-6	5	208	208	3	-4	5	305	309
12	2	4	121	117	3	4	4	164	164	4	6	4	103	100	1	-6	5	231	231	4	-4	5	234	235
-12	3	4	64	83	4	4	4	184	178	5	6	4	90	88	2	-6	5	237	246	5	-4	5	267	272
-11	3	4	81	77	6	4	4	87	76	6	6	4	122	108	3	-6	5	292	301	7	-4	5	87	90
-10	3	4	141	-132	7	4	4	94	94	7	6	4	145	149	4	-6	5	213	216	8	-4	5	414	417
-9	3	4	47	22	8	4	4	262	255	-7	7	4	80	69	5	-6	5	261	267	9	-4	5	190	185
-7	3	4	110	122	9	4	4	219	222	-6	7	4	121	-114	7	-6	5	140	143	10	-4	5	71	73
-6	3	4	250	-240	10	4	4	121	120	-3	7	4	71	74	8	-6	5	347	342	11	-4	5	111	109
-5	3	4	51	53	-11	5	4	55	-29	-2	7	4	69	-64	9	-6	5	200	200	12	-4	5	151	146
-4	3	4	154	-151	-10	5	4	47	-70	0	7	4	62	-68	10	-6	5	195	189	-10	-3	5	44	-29
-2	3	4	173	155	-9	5	4	126	-125	2	7	4	86	91	-8	-5	5	61	-52	-9	-3	5	119	135
-1	3	4	123	-115	-8	5	4	84	97	4	7	4	90	-97	-7	-5	5	104	102	-7	-3	5	74	76
0	3	4	342	-336	-6	5	4	72	-61	-5	8	4	100	92	-5	-5	5	163	-165	-6	-3	5	154	154
1	3	4	104	105	-5	5	4	68	-58	-4	8	4	198	201	-4	-5	5	41	29	-5	-3	5	295	-292
2	3	4	82	81	-4	5	4	189	188	-3	8	4	162	166	-3	-5	5	69	-57	-3	-3	5	112	106
4	3	4	65	67	-3	5	4	46	-43	-2	8	4	110	113	-2	-5	5	68	47	-1	-3	5	255	245
5	3	4	192	184	-2	5	4	159	156	-1	8	4	181	172	-1	-5	5	51	-38	0	-3	5	42	-26
6	3	4	140	148	-1	5	4	77	-78	0	8	4	133	121	0	-5	5	55	64	1	-3	5	455	446
7	3	4	145	-152	0	5	4	168	-162	-1	-8	5	158	158	1	-5	5	315	314	2	-3	5	137	139

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
3	-3	5	167	-159	13	-2	5	171	163	-1	0	5	55	60	-10	2	5	62	71	6	3	5	187	188
4	-3	5	48	-28	-12	-1	5	191	190	0	0	5	237	243	-9	2	5	120	115	7	3	5	139	-131
5	-3	5	308	-316	-11	-1	5	110	111	2	0	5	359	359	-8	2	5	489	496	8	3	5	42	-4
6	-3	5	130	-140	-10	-1	5	162	-161	3	0	5	288	299	-7	2	5	370	365	9	3	5	132	-134
7	-3	5	110	-102	-9	-1	5	172	172	4	0	5	238	237	-6	2	5	218	223	10	3	5	83	-86
8	-3	5	91	-107	-8	-1	5	98	100	5	0	5	309	316	-5	2	5	432	444	-12	4	5	79	79
9	-3	5	47	-33	-7	-1	5	77	-72	6	0	5	317	320	-4	2	5	159	171	-11	4	5	169	168
10	-3	5	229	224	-6	-1	5	129	122	7	0	5	221	221	-3	2	5	476	483	-10	4	5	120	106
11	-3	5	54	52	-5	-1	5	301	-302	8	0	5	239	240	-2	2	5	264	261	-9	4	5	89	86
12	-3	5	66	68	-4	-1	5	238	-222	9	0	5	230	222	-1	2	5	467	467	-8	4	5	373	366
13	-3	5	72	50	-3	-1	5	104	106	10	0	5	90	103	0	2	5	213	231	-7	4	5	284	287
-12	-2	5	268	272	-2	-1	5	145	-144	11	0	5	56	43	1	2	5	372	361	-5	4	5	95	100
-11	-2	5	103	96	-1	-1	5	180	-172	12	0	5	233	231	2	2	5	384	380	-4	4	5	215	221
-10	-2	5	93	84	0	-1	5	128	-122	13	0	5	142	146	3	2	5	439	435	-3	4	5	170	169
-9	-2	5	200	203	1	-1	5	49	28	-11	1	5	67	77	4	2	5	282	278	-2	4	5	319	321
-8	-2	5	179	176	2	-1	5	198	204	-10	1	5	316	-305	5	2	5	285	299	-1	4	5	172	181
-7	-2	5	335	324	3	-1	5	250	-248	-8	1	5	101	107	6	2	5	280	280	0	4	5	232	237
-6	-2	5	200	206	4	-1	5	73	-93	-6	1	5	62	-58	7	2	5	212	211	1	4	5	140	132
-5	-2	5	475	481	6	-1	5	40	-19	-5	1	5	115	116	8	2	5	170	179	2	4	5	309	298
-4	-2	5	315	314	7	-1	5	88	99	-4	1	5	78	-76	9	2	5	212	207	3	4	5	184	190
-3	-2	5	481	474	10	-1	5	124	112	-3	1	5	211	213	10	2	5	190	182	4	4	5	165	163
-2	-2	5	453	448	11	-1	5	76	76	-1	1	5	265	-256	11	2	5	113	107	5	4	5	123	123
-1	-2	5	479	463	12	-1	5	94	-100	0	1	5	52	68	-11	3	5	116	-118	6	4	5	143	155
0	-2	5	299	302	13	-1	5	60	55	1	1	5	130	128	-10	3	5	133	-140	7	4	5	165	154
1	-2	5	338	339	-13	0	5	153	146	2	1	5	147	141	-9	3	5	205	-203	8	4	5	97	106
2	-2	5	359	347	-12	0	5	205	221	3	1	5	205	193	-8	3	5	234	225	9	4	5	174	157
3	-2	5	497	502	-11	0	5	123	124	4	1	5	117	-111	-7	3	5	134	132	-11	5	5	47	-25
4	-2	5	172	176	-10	0	5	58	-39	5	1	5	361	355	-5	3	5	225	226	-10	5	5	69	-69
5	-2	5	420	433	-9	0	5	117	114	6	1	5	141	151	-4	3	5	225	224	-7	5	5	280	284
6	-2	5	238	243	-8	0	5	344	341	8	1	5	47	41	-2	3	5	211	207	-6	5	5	195	-186
7	-2	5	263	265	-7	0	5	243	246	9	1	5	175	-177	-1	3	5	336	-342	-4	5	5	91	88
8	-2	5	377	386	-6	0	5	406	405	10	1	5	114	-93	0	3	5	281	-280	-3	5	5	105	-104
9	-2	5	324	331	-5	0	5	318	329	12	1	5	128	-124	2	3	5	229	-233	-2	5	5	44	14
10	-2	5	71	79	-4	0	5	401	417	-13	2	5	215	209	3	3	5	49	44	-1	5	5	135	-138
11	-2	5	138	136	-3	0	5	185	190	-12	2	5	202	197	4	3	5	137	-139	0	5	5	158	-160
12	-2	5	248	255	-2	0	5	425	426	-11	2	5	205	204	5	3	5	71	70	6	5	5	119	124

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
8	5	5	58	-36	3	-6	6	213	212	-10	-3	6	69	93	8	-2	6	226	222	4	0	6	301	300
-9	6	5	135	132	4	-6	6	193	194	-9	-3	6	81	66	9	-2	6	250	254	5	0	6	257	253
-8	6	5	281	272	5	-6	6	254	264	-8	-3	6	173	173	10	-2	6	268	268	7	0	6	218	221
-7	6	5	247	242	6	-6	6	235	244	-4	-3	6	122	-126	11	-2	6	174	166	8	0	6	93	81
-5	6	5	68	57	7	-6	6	132	119	-3	-3	6	53	53	12	-2	6	215	217	9	0	6	174	180
-4	6	5	272	269	8	-6	6	223	223	-2	-3	6	75	82	-11	-1	6	97	85	10	0	6	263	257
-3	6	5	305	301	9	-6	6	61	46	-1	-3	6	108	115	-6	-1	6	209	-200	11	0	6	137	140
-2	6	5	218	213	-8	-5	6	59	66	0	-3	6	323	320	-5	-1	6	65	-81	12	0	6	172	166
-1	6	5	282	282	-7	-5	6	58	-25	1	-3	6	238	240	-4	-1	6	46	-41	-10	1	6	57	61
0	6	5	157	149	-5	-5	6	56	-65	2	-3	6	116	125	-3	-1	6	159	-157	-9	1	6	68	-57
1	6	5	228	229	-4	-5	6	116	-111	3	-3	6	173	173	-2	-1	6	60	76	-8	1	6	44	58
2	6	5	229	228	-2	-5	6	136	-124	5	-3	6	72	-71	-1	-1	6	38	-26	-7	1	6	101	99
3	6	5	191	191	0	-5	6	127	131	6	-3	6	81	71	1	-1	6	98	92	-6	1	6	163	152
4	6	5	121	127	2	-5	6	66	76	7	-3	6	46	-24	2	-1	6	131	-138	-4	1	6	360	344
5	6	5	124	122	4	-5	6	113	-119	9	-3	6	95	95	3	-1	6	61	-54	-1	1	6	162	163
6	6	5	149	155	7	-5	6	105	-114	10	-3	6	154	159	4	-1	6	57	-38	0	1	6	215	-220
-6	7	5	108	-98	8	-5	6	117	-131	12	-3	6	106	101	5	-1	6	180	-173	1	1	6	45	49
-5	7	5	195	-193	-9	-4	6	134	134	-11	-2	6	134	130	6	-1	6	64	-57	4	1	6	174	179
-4	7	5	97	95	-8	-4	6	139	136	-10	-2	6	157	158	8	-1	6	150	-156	5	1	6	82	66
1	7	5	47	26	-7	-4	6	219	218	-9	-2	6	211	205	12	-1	6	75	-69	6	1	6	120	122
2	7	5	52	19	-6	-4	6	170	166	-8	-2	6	192	190	-12	0	6	173	174	7	1	6	114	111
-3	-7	6	92	101	-5	-4	6	237	242	-7	-2	6	265	268	-11	0	6	194	187	8	1	6	52	32
-1	-7	6	45	41	-4	-4	6	229	223	-6	-2	6	145	148	-10	0	6	66	74	9	1	6	47	-38
0	-7	6	70	66	-2	-4	6	308	310	-5	-2	6	161	158	-9	0	6	192	188	-12	2	6	126	121
2	-7	6	79	88	-1	-4	6	210	217	-4	-2	6	223	212	-8	0	6	169	178	-11	2	6	194	200
5	-7	6	120	120	0	-4	6	267	261	-3	-2	6	122	112	-7	0	6	222	231	-10	2	6	226	210
6	-7	6	99	101	1	-4	6	255	258	-2	-2	6	298	302	-6	0	6	86	85	-9	2	6	113	121
-6	-6	6	124	133	3	-4	6	285	290	-1	-2	6	202	207	-5	0	6	231	228	-8	2	6	354	369
-5	-6	6	176	183	4	-4	6	66	54	0	-2	6	269	275	-4	0	6	209	202	-7	2	6	254	250
-4	-6	6	161	155	5	-4	6	231	227	1	-2	6	286	296	-3	0	6	374	368	-6	2	6	223	226
-3	-6	6	144	128	6	-4	6	208	195	2	-2	6	184	191	-2	0	6	361	362	-5	2	6	311	305
-2	-6	6	204	192	7	-4	6	114	115	3	-2	6	256	263	-1	0	6	372	380	-4	2	6	298	289
-1	-6	6	155	155	8	-4	6	164	165	4	-2	6	374	376	0	0	6	483	499	-3	2	6	290	300
0	-6	6	307	313	9	-4	6	198	198	5	-2	6	220	213	1	0	6	383	399	-2	2	6	284	281
1	-6	6	148	150	10	-4	6	117	122	6	-2	6	341	338	2	0	6	455	459	-1	2	6	103	112
2	-6	6	206	212	11	-4	6	235	234	7	-2	6	198	204	3	0	6	261	253	0	2	6	331	320

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
1	2	6	194	198	5	4	6	261	270	-3	-5	7	77	92	-8	-2	7	47	51	-5	0	7	210	214
2	2	6	217	222	6	4	6	235	230	-1	-5	7	170	-164	-7	-2	7	120	124	-4	0	7	249	262
3	2	6	192	201	7	4	6	107	118	0	-5	7	97	84	-6	-2	7	88	83	-3	0	7	147	149
4	2	6	47	53	8	4	6	159	143	4	-5	7	77	-81	-5	-2	7	161	175	-2	0	7	135	137
5	2	6	314	305	-7	5	6	86	98	5	-5	7	79	-77	-4	-2	7	256	261	-1	0	7	228	230
7	2	6	186	182	-6	5	6	196	204	-8	-4	7	107	116	-3	-2	7	160	164	0	0	7	613	604
8	2	6	175	179	-5	5	6	57	-49	-7	-4	7	102	108	-1	-2	7	61	64	1	0	7	623	615
9	2	6	109	97	-4	5	6	119	112	-6	-4	7	151	133	0	-2	7	478	470	2	0	7	146	136
10	2	6	236	242	-3	5	6	107	114	-5	-4	7	221	215	1	-2	7	421	414	3	0	7	147	146
-10	3	6	152	-168	-1	5	6	45	30	-4	-4	7	387	382	2	-2	7	224	218	4	0	7	53	52
-9	3	6	87	-93	2	5	6	81	72	-3	-4	7	269	279	4	-2	7	47	26	5	0	7	330	345
-8	3	6	181	-187	3	5	6	145	139	-2	-4	7	82	87	5	-2	7	59	68	6	0	7	197	200
-7	3	6	97	112	-7	6	6	207	206	-1	-4	7	122	116	6	-2	7	120	117	7	0	7	202	198
-5	3	6	64	-70	-6	6	6	157	154	0	-4	7	289	292	7	-2	7	96	85	8	0	7	156	156
-2	3	6	237	-233	-5	6	6	152	147	1	-4	7	402	405	10	-2	7	159	169	9	0	7	162	162
-1	3	6	86	-87	-4	6	6	229	236	2	-4	7	242	251	11	-2	7	186	188	10	0	7	294	304
0	3	6	238	-239	-3	6	6	140	131	3	-4	7	221	227	-9	-1	7	76	-83	-9	1	7	66	-64
1	3	6	236	-235	-2	6	6	150	146	4	-4	7	212	207	-8	-1	7	80	77	-8	1	7	114	113
4	3	6	97	85	-1	6	6	97	96	5	-4	7	261	260	-7	-1	7	57	-52	-7	1	7	64	71
7	3	6	53	3	0	6	6	161	162	6	-4	7	317	328	-6	-1	7	94	-94	-5	1	7	54	70
9	3	6	90	-88	1	6	6	132	138	7	-4	7	289	293	-4	-1	7	160	-160	-4	1	7	90	79
-10	4	6	246	255	2	6	6	122	122	8	-4	7	212	204	-3	-1	7	86	87	-3	1	7	51	45
-9	4	6	110	91	3	6	6	96	85	9	-4	7	125	121	-2	-1	7	107	104	-2	1	7	116	115
-8	4	6	202	213	4	6	6	132	133	10	-4	7	203	197	1	-1	7	118	117	0	1	7	135	-130
-7	4	6	286	289	2	-7	7	93	105	-8	-3	7	131	133	2	-1	7	161	158	1	1	7	58	-54
-6	4	6	66	60	3	-7	7	70	74	-4	-3	7	153	-158	3	-1	7	238	-241	2	1	7	135	184
-5	4	6	283	292	-4	-6	7	268	264	-3	-3	7	60	57	4	-1	7	47	60	3	1	7	140	-156
-4	4	6	142	138	-3	-6	7	202	203	-1	-3	7	82	-78	5	-1	7	98	-108	4	1	7	72	-66
-3	4	6	220	221	0	-6	7	77	80	0	-3	7	75	71	6	-1	7	46	-41	5	1	7	141	150
-2	4	6	136	133	1	-6	7	104	96	1	-3	7	244	237	7	-1	7	54	58	6	1	7	56	-65
-1	4	6	104	96	2	-6	7	68	63	2	-3	7	66	70	11	-1	7	46	-10	7	1	7	140	143
0	4	6	248	251	3	-6	7	53	66	3	-3	7	84	92	-10	0	7	298	290	-10	2	7	198	193
1	4	6	224	227	4	-6	7	77	61	4	-3	7	52	39	-9	0	7	320	328	-9	2	7	138	146
2	4	6	246	257	5	-6	7	132	130	7	-3	7	148	151	-8	0	7	213	210	-8	2	7	68	47
3	4	6	176	184	6	-6	7	195	196	-10	-2	7	148	148	-7	0	7	145	144	-7	2	7	84	68
4	4	6	222	224	7	-6	7	224	226	-9	-2	7	238	235	-6	0	7	242	245	-6	2	7	49	49

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-5	2	7	200	198	-4	5	7	60	58	0	-3	8	134	-138	-5	0	8	71	85	3	2	8	207	214
-2	2	7	79	90	1	5	7	77	-50	3	-3	8	71	-68	-4	0	8	269	289	4	2	8	71	-65
-1	2	7	113	116	2	5	7	134	118	5	-3	8	95	-117	-3	0	8	134	130	5	2	8	207	198
0	2	7	455	461	4	5	7	109	-101	-8	-2	8	99	88	-2	0	8	71	79	6	2	8	150	148
1	2	7	316	307	0	-6	8	61	57	-7	-2	8	76	67	-1	0	8	344	349	-4	3	8	102	110
2	2	7	49	72	1	-6	8	73	87	-6	-2	8	63	56	0	0	8	396	406	-3	3	8	89	99
4	2	7	182	179	-4	-5	8	50	-53	-5	-2	8	100	98	1	0	8	188	185	-1	3	8	50	50
5	2	7	258	265	-3	-5	8	209	223	-4	-2	8	244	245	2	0	8	460	476	0	3	8	77	83
6	2	7	230	224	-2	-5	8	154	149	-3	-2	8	65	65	3	0	8	44	35	1	3	8	55	54
8	2	7	87	71	-1	-5	8	89	-94	-2	-2	8	53	-16	4	0	8	155	152	2	3	8	267	262
-9	3	7	61	-75	1	-5	8	58	53	-1	-2	8	351	355	5	0	8	171	185	3	3	8	128	-133
-7	3	7	53	41	2	-5	8	62	58	1	-2	8	381	388	6	0	8	154	153	4	3	8	152	-159
-6	3	7	49	-35	3	-5	8	170	173	2	-2	8	231	238	7	0	8	107	104	-6	4	8	152	149
-3	3	7	42	53	5	-5	8	118	118	4	-2	8	138	124	8	0	8	112	124	-5	4	8	259	260
-2	3	7	105	-109	6	-5	8	59	50	5	-2	8	109	117	9	0	8	169	176	-4	4	8	175	167
0	3	7	177	-176	-6	-4	8	85	91	6	-2	8	89	86	-7	1	8	85	-88	-3	4	8	145	150
2	3	7	147	145	-5	-4	8	227	225	7	-2	8	78	70	-6	1	8	154	-166	-2	4	8	124	123
3	3	7	43	-12	-4	-4	8	301	293	8	-2	8	60	52	-5	1	8	68	-63	-1	4	8	64	50
4	3	7	87	-85	-3	-4	8	110	103	9	-2	8	131	131	-4	1	8	59	-30	0	4	8	248	248
5	3	7	55	67	-2	-4	8	218	213	-8	-1	8	88	102	-2	1	8	60	-66	1	4	8	108	102
-9	4	7	178	176	-1	-4	8	115	113	-6	-1	8	65	-71	0	1	8	178	-181	2	4	8	73	68
-8	4	7	135	137	0	-4	8	120	108	-5	-1	8	53	43	1	1	8	185	180	3	4	8	168	167
-7	4	7	245	237	1	-4	8	296	302	-4	-1	8	89	86	2	1	8	240	241	4	4	8	137	143
-6	4	7	285	280	2	-4	8	199	194	-3	-1	8	50	57	3	1	8	151	-155	-2	5	8	151	-154
-5	4	7	370	376	3	-4	8	101	109	-2	-1	8	221	220	4	1	8	137	-137	-2	-4	9	80	89
-3	4	7	174	176	4	-4	8	249	245	-1	-1	8	201	-207	5	1	8	52	-41	-1	-4	9	213	209
-2	4	7	269	267	5	-4	8	209	212	0	-1	8	171	-170	6	1	8	46	-39	1	-4	9	102	123
-1	4	7	185	191	6	-4	8	237	234	1	-1	8	152	151	-8	2	8	139	131	2	-4	9	123	125
0	4	7	333	324	7	-4	8	194	183	2	-1	8	165	163	-6	2	8	168	156	3	-4	9	61	39
1	4	7	267	255	8	-4	8	101	102	5	-1	8	84	82	-5	2	8	117	112	4	-4	9	80	85
2	4	7	49	35	-6	-3	8	64	-80	7	-1	8	201	206	-4	2	8	133	129	-4	-3	9	80	59
3	4	7	130	125	-5	-3	8	68	58	9	-1	8	79	60	-3	2	8	177	185	-1	-3	9	65	-75
4	4	7	241	238	-4	-3	8	102	-94	-9	0	8	289	302	-1	2	8	221	233	0	-3	9	87	-82
5	4	7	344	344	-3	-3	8	198	210	-8	0	8	143	145	0	2	8	267	266	2	-3	9	125	-122
6	4	7	197	199	-2	-3	8	180	186	-7	0	8	110	108	1	2	8	151	157	4	-3	9	49	-68
-5	5	7	59	-57	-1	-3	8	235	-241	-6	0	8	200	191	2	2	8	95	91	5	-3	9	71	67

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
6	-3	9	119	127	4	-2	9	190	189	-4	0	9	136	135	-5	1	9	129	-136	0	2	9	152	163
-5	-2	9	150	153	5	-2	9	193	189	-3	0	9	114	117	-3	1	9	53	-54	1	2	9	86	87
-4	-2	9	134	135	6	-2	9	174	181	-2	0	9	87	84	3	1	9	47	-45	2	2	9	149	144
-3	-2	9	49	44	-5	-1	9	63	86	-1	0	9	290	302	4	1	9	71	-75	3	2	9	107	118
-2	-2	9	136	138	-3	-1	9	115	113	0	0	9	95	106	5	1	9	61	-56	4	2	9	128	117
-1	-2	9	161	164	-2	-1	9	62	71	1	0	9	188	189	-5	2	9	104	106	-4	3	9	104	-118
0	-2	9	180	166	-1	-1	9	61	48	2	0	9	135	145	-4	2	9	237	241	-3	3	9	73	85
1	-2	9	60	53	4	-1	9	85	85	3	0	9	210	219	-3	2	9	173	178	-1	3	9	60	72
2	-2	9	313	318	6	-1	9	126	125	5	0	9	125	130	-2	2	9	152	149	0	3	9	56	70
3	-2	9	108	101	-5	0	9	75	59	6	0	9	109	123	-1	2	9	212	203	1	3	9	73	77

APPENDIX B

THE CONSISTENCY OF WEIGHTS

It is possible to test the consistency of a weighting scheme by considering the standard deviation, S, of a reflection of unit weight. The SHELX programme provides a table of variance values defined as:

$$V = 100 * S = 100 * [M * \sum_{1}^{N}(w)(F - F_c)^2/N * \sum_{1}^{M}(w)]^{\frac{1}{2}}$$

where N is the number of reflections in the group, M is the total number of reflections and w is the weight factor. These values are presented in Table B.1. If the weights are satisfactory, it is expected that S would be distributed as $\chi^2/(n - m)$ for n - m degrees of freedom (1). That is,

$$\frac{\chi^2_{n-m,\ 1-\alpha}}{n-m} < S < \frac{\chi^2_{n-m,\ \alpha}}{n-m}$$

In this structure, there are 2390 observations defining 397 variables and therefore 2390 - 397 = 1993 degrees of freedom. For more than 100 degrees of freedom, the values of $\chi^2_{n-m,\ 0.99}$ may be approximated by the expression (2): $\frac{1}{2}[(2(n - m) - 1)^{\frac{1}{2}} + 2.33]^2$. Thus,

$$\chi^2_{1993,\ 0.99} = \frac{1}{2}[(2 * 1993 - 1)^{\frac{1}{2}} + 2.33]^2 = 2142$$

and

$$\frac{\chi^2_{1993,\ 0.99}}{1993} = 1.07$$

---

1. W. C. Hamilton in International Tables for X-ray Crystallography, Vol. IV, the Kynoch Press, Birmingham, England (1974). p 293.

2. E. Kreyszig, Advanced Engineering Mathematics , 3rd ed., John Wiley and Sons, Inc., Toronto, Canada (1972). p 843.

Similarly,

$$\chi^2_{1993,0.01} = \frac{1}{2}[(2 * 1993 - 1)^{\frac{1}{2}} - 2.33]^2$$
$$= 1848$$

and

$$\frac{\chi^2_{1993,0.01}}{1993} = 0.93$$

Therefore, the condition, $0.93 < S < 1.07$, should hold.

From the table of values produced by SHELX (Table B.1), it can be seen that S = 0.95 for all the data. From this, it was concluded that the overall weighting scheme was satisfactory. However, the value of S should also be independent of the choice of subset and this criterion is not fully satisfied. In the following paragraphs, possible causes for a number of the values outside the desired range are discussed.

First of all, the value of S appears to be correlated to the parity of k. Reflections with even k values tend to have S less than 0.93. In other words, the odd k reflections have been systematically overweighted. This correlation is a result of the pseudosymmetry with respect to the y axis but it was not thought to be a serious problem.

As expected, there is no systematic distinction between the data collected from 0° to 35° and the set, 35° to 45°, which was collected later (see SIN THETA table). However, low angle reflections, which are generally more intense as well, tend to be somewhat overweighted. This correlation was thought to result from the fact that no corrections were made for extinction. Intense, low angle reflections are particularly susceptible to extinction which is due to multiple internal reflections of the x-rays. However, after examination of observed and calculated

structure factors, it was found that extinction affected very few, if any, reflections. Therefore, either extinction has not caused the correlation or, if it has, the effect is very small.

As a third group, the weaker reflections seem to be underweighted (see SQRT(F/FMAX) table). This implies that σ is large for these reflections which is to be expected since σ varies as $1/\sqrt{I}$ where I is the relative intensity.

In conclusion, the overall weighting scheme was termed satisfactory and apparent systematic deviations were not of sufficient magnitude to warrant further revision.

Table B.1

ANALYSIS OF VARIANCE FOR BIS(PYRIDOXAMINE)COPPER(II) NITRATE.H2O

	GGG	UGG	GUG	UUG	GGU	UGU	GUU	UUU	ALL
N	351	343	237	240	351	352	264	252	2390
V	90	91	111	119	84	82	101	94	95

SIN THETA 0.00 - 0.17 - 0.22 - 0.25 - 0.28 - 0.30 - 0.32 - 0.34 - 0.36 - 0.37 - 0.39

N	242	270	217	291	216	235	271	311	146	191
V	122	112	94	83	83	94	90	84	84	95

SQRT(F/FMAX) 0.00 - 0.19 - 0.22 - 0.25 - 0.28 - 0.30 - 0.33 - 0.37 - 0.41 - 0.47 - 1.00

N	309	237	238	261	184	221	290	206	216	228
V	117	104	102	96	103	91	84	81	76	83

ABS(H)	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	116	237	228	227	233	213	197	173	170	153	130	115	90	59	49
V	99	92	98	100	100	90	96	104	90	97	86	94	97	78	92

ABS(K)	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	224	348	435	302	371	216	253	111	114	16	0	0	0	0	0
V	87	113	88	108	82	96	88	99	90	104	0	0	0	0	0

ABS(L)	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	158	392	360	331	306	274	219	160	128	62	0	0	0	0	0
V	135	99	105	88	93	83	84	79	83	85	0	0	0	0	0